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THERMOCHEMICAL CALCULATIONS

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THERMOCHEMICAL CALCULATIONS

BY

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THERMOCHEMICAL CALCULATIONS

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PREFACE

Another addition to the already well-developed field of thermodynamics might be regarded as so much useless repetition if it were not for the following significant statement in the preface to the textbook on thermodynamics by Lewis and Randall: "There are several kinds of audience to which a book on thermodynamics might be addressed. There is the beginner who, in order that he may decide whether the subject will meet his needs or arouse his interest, asks what thermodynamics is and what sorts of problems in physics, chemistry, and engineering can be solved by its aid; there is the reader who looks for the philosophical implications of such concepts as energy and entropy; *above all there is the investigator who, attacking problems of pure or applied science, seeks the specific thermodynamic methods which are applicable to his problem and the data requisite for its solution.*" In the opinion of the author none of the textbooks available today adequately fulfills the needs of this last group. It is with this in mind that the reader should view the somewhat unorthodox presentation and subject matter of this volume.

The book is not intended to be a comprehensive presentation of the principles of thermodynamics, nor is it intended to be a textbook of industrial chemistry or chemical engineering since these subjects have been sufficiently discussed in books bearing these titles. It is true, however, that in textbooks of thermodynamics scant attention has been paid to the presentation of methods for applying thermodynamics to practical problems; similarly, books on industrial chemistry and chemical engineering devote little space to the use of thermodynamics in solving concrete technological problems. The material here presented represents an attempt to make up for these deficiencies by demonstrating methods for applying thermodynamic principles to a wide variety of practical laboratory and technological problems. It would be unreasonable to expect a single author to produce a comprehensive work on all three subjects and it would hardly be desirable from the teaching standpoint. An effort has been made,

nevertheless, to make the volume reasonably self-contained with respect to thermodynamic material of primary interest to chemists and chemical engineers engaged in academic or industrial work.

Another equally important object has been the presentation of practical methods for computing thermodynamic functions provided by statistical and quantum mechanics and developed during the last decade. Although these procedures belong in the domain of the theoretical physicist and chemist, the modern chemist or technologist of average mathematical attainments should be able to master the more useful procedures. The importance of other recent theoretical developments in the field of molecular structure and their bearing on the thermodynamic properties of matter have also been discussed in the appropriate sections.

In order to facilitate thermodynamic analyses of systems for which a portion of the requisite thermal data is missing, a number of methods are presented for estimating various items of thermodynamic data which have been found useful in the author's experience. These methods should be used for what they are worth and only after all the usual sources of data have failed to provide the necessary experimental values. Complete elimination of the preliminary thermodynamic analysis of a problem cannot be justified on the grounds of an otherwise praiseworthy penchant for accuracy, merely because of the absence of a heat of fusion which may be roughly estimated.

It is believed that the material presented in the following pages might serve as a fifth or sixth year course for students in chemistry or chemical engineering to supplement previous standard courses in thermodynamics and the unit operations of chemical engineering. The research chemist or engineer with a good background in general physical chemistry, including the first and second laws of thermodynamics, should be able to handle the subject matter with the help of the indicated collateral reading. A section containing 60 unsolved problems for classroom or individual work has been included at the end of the book. Since actual problems arise in laboratory or plant investigations without regard for the order of subject presentation in textbooks, no attempt has been made to arrange these problems to correspond to the arrangement of the various topics in the text. The last

18 problems are, however, arranged to require considerable searching of the literature for the necessary data in order to familiarize the student with the best and most modern sources of data in the field.

Since errors are almost unavoidable, it is hoped that they are not too numerous or too serious and that the reader will call attention to them.

RALPH R. WENNER.

WINTERDALE, PA.,
July, 1941.

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NOTE: Boldface section numbers indicate solved problems.

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PART I
PRINCIPLES

CHAPTER I

SCOPE, DEFINITIONS, AND UNITS

1. Scope.—The importance of a thorough knowledge of the fundamentals of thermodynamics to the modern chemist or chemical engineer has been adequately set forth in the numerous textbooks of physical and chemical thermodynamics that have appeared in the last 20 years. Although these texts leave little to be desired from the standpoint of clarity and thoroughness of exposition of the basic principles governing the equilibriums of physical and chemical changes, little attention has been paid to the elucidation of the technique of applying these principles to the practical problems of chemistry and technology.

One very good reason for this deficiency is that most technological problems do not deal with systems in equilibrium; hence it would appear to be impossible to divorce any concrete applications of thermodynamic principles from equally important considerations involving rates of reactions, rates of heat transfer, rates of mass transfer, etc. On this basis much of the material presented on subsequent pages may not appear to belong in the province of thermodynamics, although it is hoped that no flagrant violations of the basic tenets of this science have been committed. In many cases equilibrium conditions will be regarded as limiting conditions of systems in which net simultaneous thermal, physical, and chemical changes are taking place. Such systems are termed “productive” systems, in contradistinction to equilibrium or nonproductive systems in which no net changes may take place unless the usual variables determining the state of the system are deliberately altered. The results of a thermodynamic analysis of an assumed productive system possess much more technical significance than those based on an idealized nonflow system which is assumed to be uniform in composition and temperature throughout. This is particularly true of metallurgical processes where the temperature and concentration gradients are so large as to render the results of analyses obtained on the basis of uniform conditions of little practical significance.

A type of productive system that may advantageously be analyzed with the aid of thermodynamics is one in which localized equilibria are established at phase interfaces. For example, the design of equipment used in gas absorption and extraction operations is based on the concept that the net rate of absorption or extraction, at any point, is controlled by rates of diffusion through substantially stationary films of solvent situated on both sides of the interface, and that true physical and chemical equilibrium exists at the interface between the two phases only. Since the rate at which matter is transferred from one phase to another is determined by the concentration gradients existing across each film, it is apparent that a quantitative knowledge of the equilibria established at phase interfaces is important in design considerations.

No justification is offered for the omission of certain topics usually included in most textbooks of thermodynamics or for the inclusion of others that are usually omitted. Thus, although the subject of fluid flow is important to both the chemist and the chemical engineer dealing with flow systems, and although the first and second laws of thermodynamics constitute the basis for the quantitative treatment of steady-flow problems, this subject is usually omitted from academic treatises on thermodynamics. The main purpose of the author has been to collect the most important methods or tools available for use in the field of thermodynamics and to demonstrate, by means of solved problems, their application to a wide variety of problems encountered in various branches of technology.

In certain cases the subject matter of a problem may not appear to warrant its inclusion under the heading of applied thermodynamics. However, examination of these problems will reveal that, in all cases, enthalpy changes are involved and, as a general rule, an equilibrium state is involved—if only under some of the special conditions mentioned above. For these reasons, the present volume has been entitled “Thermochemical Calculations,” rather than “Thermodynamic Calculations.”

Since it is assumed that the reader has already been exposed to some formal exposition of the principles of thermodynamics, an elaborate repetition of well-developed theoretical concepts is omitted. It will be noticed that the book has been divided into two parts: the first eight chapters are devoted to a brief presenta-

tion of principles and their applications to thermodynamic problems, and the last nine chapters are devoted to the applications of these principles to practical technological problems.

It has been considered advisable to expand the usual treatment of partial molar-heat capacities and heat contents of aqueous solutions in order to include the modern method of computing and correlating the results of experimental investigations in this field. The chapter on enthalpy changes accompanying chemical reactions also attempts to present some of the more recent experimental and theoretical developments in this very important branch of thermodynamics.

Since the more useful thermodynamic functions of a system may be computed from a knowledge of (1) the heat capacities of the individual components of the system between the absolute zero and the temperature in question, (2) the enthalpy changes accompanying changes in state occurring between these two temperatures, and (3) the standard heats of formation of each component at some definite temperature, an effort has been made to include all useful theoretical or empirical procedures available for estimating any of these functions, as well as entropies. The use of molecular structure and spectroscopic data for the computation of thermodynamic functions is discussed in some detail. These methods are presented in Chaps. VII and VIII.

The absence of special treatment of *PVT* (equation of state) data for pure liquids and gases and *PVT*-composition data for solutions may be considered unfortunate. The omission is due, however, to the fact that comprehensive treatments of the subject for pure components are available in several books, whereas the treatment of multicomponent systems is still largely empirical. A number of problems involving the use of different equations of state and correlations of thermodynamic functions in terms of the reduced temperature and pressure are presented throughout the text.

2. Fundamental Concepts.—The following discussion is concerned chiefly with the definition of four fundamental thermodynamic functions of particular interest to the chemist. Subsequent applications of these functions will do more toward clarifying their significance than many pages of descriptive matter.

a. Energy.—When a quantity of heat Q is absorbed by a system at the same time the system performs a quantity of work W against mechanical, gravitational, electrical, or magnetic forces, the increase in energy of the system in passing from the initial state (1) to the final state (2) is given by the relation

$$\Delta E = Q - W = E_2 - E_1. \quad (1.1)$$

This statement serves simultaneously as the definition of energy and as the first law of thermodynamics. Energy is a function of the state of the system only. In most thermochemical considerations the work done on or by the system is mechanical, and, if reversible, is given by the expression

$$W = \int_{V_1}^{V_2} P dV \quad (1.2)$$

where P and V represent the pressure and volume of the system, respectively.

A system is said to undergo a reversible process when it can be restored to its initial state without producing any resultant change in the conditions that originally existed in the surroundings. For the process to occur reversibly, it is necessary that no sensible temperature, pressure, concentration, or potential gradients occur at any stage of the process.

b. Enthalpy or Heat Content.—Substituting Eq. (1.2) in (1.1) and integrating for a constant-pressure process yield the relation

$$Q = E_2 - E_1 + P(V_2 - V_1) = E_2 + PV_2 - (E_1 + PV_1). \quad (1.3)$$

Thus, if the function of the state of the system represented by $E + PV$ is called the enthalpy or heat content H , then the increase in enthalpy experienced by the system in passing from state (1) to state (2), under constant pressure, equals the heat absorbed by the system. In general, the increase in enthalpy for processes occurring under any conditions of temperature and pressure is given by the equation

$$\Delta H = \Delta E + \Delta(PV). \quad (1.4)$$

c. Entropy.—When a quantity of heat dQ is absorbed at the absolute temperature T , under reversible conditions, the increase in entropy is given by the relation

$$dS = \frac{dQ}{T}. \quad (1.5)$$

For any spontaneously occurring process

$$dS > \frac{dQ}{T}, \quad (1.6)$$

and for a nonspontaneous process

$$dS < \frac{dQ}{T}. \quad (1.7)$$

As in the case of energy and enthalpy, entropy is a point function, *i.e.*, it depends only on the state of the system.

Equations (1.5) to (1.7) constitute one mode of expressing the second law of thermodynamics. In its most generally useful form, this law states: *A process in which the final result is only a transformation of heat into work is an impossibility.* Although the equivalence of these two statements of the second law is not obvious, a clear, elementary discussion of the equivalence may be found on pages 105–115 of Noyes and Sherrill.¹

Substituting Eq. (1.5) in Eq. (1.1) gives the following combined statement of the first and second laws for an infinitesimal, reversible process involving mechanical work only:

$$dE = TdS - PdV. \quad (1.8)$$

d. Free Energy.—Still another function of the state of a system exists which is of major interest to the chemist, since it permits the prediction of equilibrium conditions for physical and chemical changes. It represents the maximum nonmechanical work theoretically obtainable from processes occurring at constant temperature and pressure. This function is called the “free energy.” The increase in free energy in going from the initial to the final state of the system is given by the equation

$$\Delta F = \Delta H - T\Delta S. \quad (1.9)$$

The quantity $T\Delta S$ is sometimes called the “irreversible energy,” sometimes the “reversible heat,” and sometimes the “latent heat” of the process. Actually, it represents the heat that must be absorbed or given up to the surroundings during the reversible

¹ See corresponding item in References at end of this chapter.

process, which yields the free-energy change ΔF , in order to maintain isothermal conditions. It should be noted that the ΔH of a process is related to the entropy change through Eq. (1.9), and that the enthalpy change divided by the temperature is equal to ΔS only when ΔF equals zero.

Although chemists and engineers are occasionally interested in computing the maximum amount of useful work obtainable from a cell reaction, or the minimum amount of energy required to effectuate a definite cell process, the principal use of data on free-energy changes is for the computation of equilibrium constants K , by means of the relation

$$\Delta F^\circ = -RT \ln K. \quad (1.10)$$

As the process of developing the numerical application of this relation to concrete problems becomes clearer, it will be noticed that the problem of computing K under any set of conditions resolves itself into the evaluation of the three items mentioned in the next to the last paragraph of Sec. 1. Although in some cases the procedure may be varied somewhat, the present trend in experimental thermodynamics is in the direction of the development of more and better values for heats of formation and entropies of substances from measured or computed heat capacities.

Further interpretation of the significance of the above functions will be reserved for the chapters dealing with the use of these and derived relations for the solution of definite thermochemical problems. It should be emphasized at the outset that correct formal application of sound thermochemical data does not guarantee results capable of being checked in either the laboratory or the plant. A thoroughgoing qualitative knowledge of the chemistry of the main reactions involved, as well as possible secondary reactions, should be established in advance of any attempt to derive a quantitative picture of the system, if significant results are to be obtained. Furthermore, a preliminary qualitative picture of the thermal stability of the various reactants and products is highly important, since, at elevated temperatures, compounds possessing positive free energies of formation may or may not tend to decompose into their constituent elements. For example, thermodynamics predicts that such compounds as benzene and hydrogen cyanide should be entirely decomposed

into the elements under the conditions of most reactions involving these substances. That such is not the case is due, of course, to the inability of thermodynamics to predict the rate at which a system will attain a definite possible level of stability, and which level will be ultimately reached within a reasonable period of laboratory observations or plant operations. Frequently, the ultimate level of stability attained may depend on the presence or absence of various catalytic substances from the system; hence, the need for the judicious use of old-fashioned textbooks of chemistry, along with correct thermodynamic treatment, is apparent.

3. Definitions of Units.—The definitions of some of the more common units employed throughout the text are given below for convenience:

a. The *dyne* is the unit of force that will impart to a freely moving mass of one gram an acceleration of one centimeter per second per second.

b. The *erg* is the work done by a force of one dyne, acting through a distance of one centimeter.

c. One *joule* equals 10^7 ergs. The product of absolute amperes by absolute volts by seconds gives the energy expended in an electrical circuit in absolute joules.

d. One 15° *calorie* (cal.) equals 4.185 absolute joules equals 4.1833 international joules. Since the heat capacity of water⁴ in the interval 15 to 16°C . equals 4.185 absolute joules per degree centigrade per gram, the calorie represents the heat required to raise one gram of water one $^\circ\text{C}$. in this interval. The maximum variation in the heat capacity of water from this value, in the range 0 to 100°C ., is less than 0.8 per cent.

e. The *international steam-table calorie* (It. cal.) equals $\frac{1}{860}$ international watt-hours.

f. The *centigrade heat unit* (C.h.u.) equals the heat required to raise one pound of water one degree centigrade, or 453.6 calories. This unit is also called the pound centigrade unit.

g. The *British thermal unit* (B.t.u.) equals the heat required to raise one pound of water one degree Fahrenheit, or 252 calories, or 778.3 foot-pounds.

h. The gas constant *R* has the following values in various systems of units (unless otherwise specified, the gram mole is understood):

| Units | <i>R</i> |
|---|----------|
| Joules per mole per degree centigrade | 8 314 |
| Calories per mole per degree centigrade | 1.987 |
| B.t.u. per pound mole per degree Fahrenheit. | 1.987 |
| <hr/> | |
| Liter-atmospheres per mole per degree centigrade | 0 08205 |
| Cubic feet-atmospheres per pound mole per degree centigrade | 1 315 |
| Foot-pounds per pound mole per degree Fahrenheit | 1.543 |
| Foot-pounds per pound mole per degree centigrade | 2,780 |

i. The *faraday constant* (*F*) equals the quantity of electricity required to precipitate one gram mole of a singly charged ion, or 96,494 coulombs.

j. The *volt equivalent* equals the energy change associated with the transfer of one gram mole of singly charged ions through a potential difference of one volt, or 23,066 calories.

k. The *freezing point* of water on the absolute centigrade scale will be taken equal to 273.1°K., although the value 273.16°K. is undoubtedly more accurate. This choice is based on the fact that the bulk of the best critical thermodynamic data, particularly the compilations of K. K. Kelley, are referred to 273.1°K.

In general, the nomenclature of Lewis and Randall² has been employed throughout the text. The symbols *l*, *g*, and *c* have been used to designate the liquid, gaseous, and macrocrystalline states, respectively. In view of the fact that the treatise on thermodynamics by Lewis and Randall and the compilation of thermochemical data by Bichowsky and Rossini³ are cited so frequently, the abbreviations L-R and B-R, respectively, have been used to designate these references.

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CHAPTER II

THERMAL EFFECTS ACCOMPANYING PHYSICAL CHANGES OF STATE

1. Heat Capacities at Constant Volume.—From the statement of the first law of thermodynamics in the form that

$$\Delta E = Q - W = Q - \int_{V_1}^{V_2} P dV, \quad (2.1)$$

it follows that $W = 0$ for any process occurring at constant volume and, therefore, the heat absorbed equals the increase in internal energy of the system. The limit of the ratio of the increase in internal energy of the system to the corresponding increase in temperature accompanying an infinitesimal absorption of heat is called the "heat capacity at constant volume"; thus

$$C_v = \frac{dE}{dT}. \quad (2.2)$$

Obviously, the magnitude of C_v will depend on the quantity of material considered. When dealing with a unit weight of a substance, small c is employed; and this ratio is then called the "specific heat." Capital C is used to designate the heat capacity of the gram or pound mole of a substance. Since most actual processes are carried out under constant pressure, the heat capacities at constant pressure possess greater usefulness than those at constant volume.

2. Heat Capacities at Constant Pressure.—From the equation defining the increase in enthalpy for processes taking place at constant pressure,

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V, \quad (2.3)$$

and the first law, it follows that

$$\Delta H = Q; \quad (2.4)$$

consequently the increase in heat content equals the heat absorbed at constant pressure. The limit of the ratio of the

increase in heat content of the system to the corresponding increase in temperature for an infinitesimal absorption of heat under these conditions is called the "heat capacity at constant pressure" and is defined by the equation

$$C_p = \frac{dH}{dT}. \quad (2.5)$$

Equation (2.5) will be found essential in the solution of such diverse problems as the calculation of pressure drops in fluid-flow considerations, the design of heat interchangers for heating or cooling reaction mixtures, the prediction of the variation of theoretical reaction conversions with temperature, the variation of heats of physical and chemical changes with temperature, and the computation of theoretical maximum flame temperatures attainable by the combustion of gases of known composition.

3. Heat Capacities of Gases.—At pressures not much greater than atmospheric most gases behave in accordance with the equation

$$PV = RT, \quad (2.6)$$

and a simple relation may then be shown to exist between the molar-heat capacities at constant volume and constant pressure. By substituting RT for PV in the equation defining enthalpy, differentiating with respect to T , and substituting Eqs. (2.2) and (2.5) for the differential coefficients, the relation

$$C_p - C_v = R \quad (2.7)$$

is obtained.

On the basis of old-fashioned kinetic theory, gas molecules resemble rigid dumbbells or spheres, possessing three translational degrees of freedom in the x -, y -, z -directions, plus two (linear molecules) or three rotational degrees of freedom, corresponding to rotation about principal axes at the center of gravity of the molecule. According to the principle of equipartition of energy, the average kinetic energy associated with each degree of freedom is $RT/2$ per mole, and the heat capacity associated with each degree of freedom is $R/2$. On this basis, the molar-heat capacity of gases should be independent of temperature. For diatomic or linear molecules the molar-heat capacity is

$$C_p = 5 \left(\frac{R}{2} \right) + R = 6.96 \text{ cal./(g. mole)(deg. C.)}; \quad (2.8)$$

and for polyatomic molecules with three rotational degrees of freedom

$$C_p = 6 \left(\frac{R}{2} \right) + R = 7.95 \text{ cal.}/(\text{g. mole})(\text{deg. C.}). \quad (2.9)$$

Actually, it is found that, except for low temperatures, these values represent lower limits to the heat capacities, and that the observed heat capacities increase regularly with temperature, in accordance with the equation

$$C_p = a + bT + cT^2, \quad (2.10)$$

or, as suggested by Kelley,¹

$$C_p = a + bT - cT^{-2}. \quad (2.11)$$

Furthermore, it has been found that only the heat capacities of monatomic gases conform to these simple considerations, and sometimes, as in the case of gaseous metallic atoms at elevated temperatures, predicted values may be exceeded. For monatomic gases possessing no rotational degrees of freedom,

$$C_p = 3 \left(\frac{R}{2} \right) + R = 4.97 \text{ cal.}/(\text{g. mole})(\text{deg. C.}). \quad (2.12)$$

Since, at most temperatures, the actual heat capacities are greater than the values predicted by simple equipartition theory, it must be concluded that molecules have internal degrees of freedom that contribute to the total heat capacity, as well as translational and rotational degrees of freedom. These additional degrees of freedom are known to reside in the internal vibrations of the constituent atoms of the molecule, in the internal rotations of groups of atoms about single bonds joining these groups, and in the motions of the extranuclear electrons surrounding the nuclei of the constituent atoms. For all practical purposes the heat capacity associated with translational and external rotational degrees of freedom may be assumed equal to the equipartition value for all but very low temperatures; consequently, fairly accurate heat capacities may be computed by adding the contributions from these internal degrees of freedom to the appropriate Eq. (2.8), (2.9), or (2.12). Since these internal degrees of freedom can possess energy only in definite, discrete (quantized) values, the theoretical computation

of heat capacities, and other thermodynamic functions of such systems, requires special statistical mechanical application of data, usually obtained from spectroscopic studies. The method of utilizing such data for thermodynamic purposes will be discussed in Chap. VII.

For the reader's convenience, Appendix I contains a number of equations expressing molar-heat capacities as a function of the absolute temperature for some of the more common gases. Since most textbooks express heat capacities as a simple power series in T [Eq. (2.10)], and Kelley¹ finds that experimental data fit an equation of the form of (2.11) more closely, both equations are given when available.

4. Heat Capacities of Solids.—No simple, adequate theory exists for computing heat capacities of solid substances. In the case of solid elements, the classical equipartition principle predicts an average kinetic energy of $RT/2$ associated with each of the three degrees of translational freedom, plus an equal amount of potential energy due to displacements of the atoms from their equilibrium positions in the lattice. Thus the heat capacity at constant volume should equal

$$C_v = 3 \left(\frac{R}{2} \right) + 3 \left(\frac{R}{2} \right) = 5.96 \text{ cal./(g. mole)(deg. C.)}. \quad (2.13)$$

As a matter of experimental fact, most solid elements, with the exception of highly electropositive elements, approach this value at high temperatures. For compound substances it is customary to assume, as a rough approximation, that each atom has its equipartition value; thus, the molar-heat capacity equals $5.96n$, where n is the number of atoms in the molecule. For solids, the heat capacity at constant pressure may be computed from the constant-volume value by means of the equation,

$$C_p - C_v = \frac{\alpha^2 VT}{\beta}, \quad (2.14)$$

where α = coefficient of thermal expansion.

β = coefficient of compressibility.

V = molar volume.

Since this difference is usually less than 0.5 cal./g. atom near room temperature, the molar-heat capacity at constant pressure is computed as $6.2n$ (Kopp's law). Experimental results indi-

cate that, in computing the heat capacities of solids containing these elements, the following average values should be assigned: $C = 1.8$, $H = 2.3$, $B = 2.7$, $Si = 3.8$, $O = 4.0$, $F = 5.0$, $P = 5.4$, and $S = 5.4$.

It will be noted that the classical equipartition theory predicts values of C_v for solids, which should be independent of temperature. At ordinary temperatures this is approximately the case; at low temperatures the heat capacities of solids decrease rapidly with decreasing temperature. In an attempt to evolve a more realistic theory of specific heats of solids, Debye² has treated atomic solids as continuous, elastic bodies possessing $3N$ modes of vibration, corresponding to the usual $3N$ degrees of freedom of a system containing N atoms. The energy content of such a solid is obtained by setting up an expression for the number of modes of vibration lying in a given frequency range, and assigning to each mode the Einstein value for the average energy of a quantized harmonic oscillator of frequency ν , and integrating over the volume of the solid from zero to a maximum frequency determined by the elastic properties of the solid.

The heat capacities predicted by this theory become proportional to the cube of the absolute temperatures at low temperatures and are equal to the equipartition value $3R$ (law of Dulong and Petit) at high temperatures—in agreement with experiment. The energy content and heat capacity of a Debye solid become a function of a single parameter called the “characteristic temperature,” which is best determined by a reliable heat-capacity measurement at a temperature so low that the heat capacity of the solid has fallen to about half the equipartition value. Having once determined θ_D , the heat-capacity curve may then be computed down to the absolute zero with the help of tables of Debye functions. Unfortunately, the Debye theory can be applied accurately only to atomic solids; and it is employed chiefly as a tool for extrapolating heat capacities measured in a convenient experimental region down to very low, inaccessible temperatures. Modifications of the Debye theory, developed by Nernst and by Born and vonKármán, are useful in estimating the heat capacities and entropies of compound substances. These methods will be discussed in Chap. VII.

5. Heat Capacities of Liquids.—Developments in the theory of the liquid state by Eyring and others³ have not reached a stage

where it is possible to predict heat capacities of liquids. In general, the experimental results indicate that the heat capacity of a substance in the liquid state is somewhat greater than in the solid state. Accordingly, where actual measured values are not available, it will be convenient to assume the heat capacity at constant pressure equal to 8 cal./(*g.* atom)(deg.) in the liquid state. Molar-heat capacities may then be taken equal to $8n$, where n represents the number of atoms in the molecule. Molecules containing the following atoms should be modified as follows: C = 2.8, H = 4.3, B = 4.7, Si = 5.8, O = 6.0, F = 7.0, P = 7.4, and S = 7.4.

The heat capacities of liquid solutions are not, in general, related in a simple manner to the heat capacities of the pure components. The heat capacity of a binary solution may be computed from the relation (L-R, p. 83),

$$C_p = n_1 \bar{C}_{p_1} + n_2 \bar{C}_{p_2}, \quad (2.15)$$

where n_1 and n_2 represent the moles of components 1 and 2, respectively, and the partial molar-heat capacities are defined by the equations

$$\bar{C}_{p_1} = \frac{\partial C_p}{\partial n_1} \quad \text{and} \quad \bar{C}_{p_2} = \frac{\partial C_p}{\partial n_2}. \quad (2.16)$$

That is, the partial molar-heat capacity of component 1 represents the increase in heat capacity of the solution per mole of component 1, accompanying the addition of an infinitesimal quantity of 1—all other variables remaining constant. Lewis and Randall (L-R, p. 36) describe four different methods for evaluating partial molar quantities from the observed dependence of that property on concentration. A few binary solutions exist for which the heat capacity is a simple linear function of the molar-heat capacity of the pure components, as expressed by the equation (so-called "ideal solutions")

$$C_p = N_1 C_{p_1} + N_2 C_{p_2}, \quad (2.17)$$

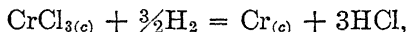
where the N 's represent mole fractions.

Dilute solutions of nonelectrolytes in water, such as urea, dextrose, and glycerin, obey this relation fairly well; but such cases are the exception rather than the rule. In the case of solutions of electrolytes in water, the heat capacities are usually less

than that of pure water. When actual experimental data are lacking for dilute aqueous solutions of electrolytes, the heat capacity per gram may be estimated by taking the specific heat equal to the weight fraction of H_2O in the solution. For example, the specific heat of a 21.6 weight-per cent solution of NaCl in water at 25°C . is 0.806 cal./deg., whereas this rule would give a value of 0.784. A more extensive treatment of the heat capacities of aqueous solutions is presented in Chap. III, in the discussion of the closely related subject of heats of solution.

6. Calculation of Heat Required for Preheating Reactants.

Illustration 1.—Metallic chromium may be recovered from chromite ore by treatment with Cl_2 , followed by separation of the iron and chromic chlorides by distillation, and the reduction of the chromic chloride with hydrogen. Assuming that the over-all result of the reduction treatment is represented by the equation



and that this reaction proceeds at a practical rate at 900°C ., what is the minimum quantity of heat required per ton of chromium in order to preheat the reactants to 900°C .? Assume that the reaction could be carried out in a continuous counter-current reactor with 50 per cent efficient utilization of the H_2 .

Solution.—Neglecting heat losses, the minimum heat required for the preheating operation under 1 atm. pressure is the increase in enthalpy of the reactants when heated from ordinary temperature (25°C .) to the reaction temperature (900°C .).

$$\begin{aligned}\text{Pound moles of Cr required} &= \frac{2,000}{52.01} = 38.4 \\ &= \text{pound moles, CrCl}_3.\end{aligned}$$

$$\text{Pound moles of H}_2 \text{ required} = (2)(1.5)(38.4) = 115.2 \text{ lb. moles.}$$

The heat capacity of H_2 , as given by Kelley,¹ is

$$C_p = 6.62 + 0.81 \cdot 10^{-3}T.$$

Unpublished data cited by Doerner⁴ for the heat capacity of solid CrCl_3 may be employed:

$$C_p = 19.44 + 7.03 \cdot 10^{-3}T.$$

Hence the centigrade heat units required to raise 38.4 lb. moles of CrCl_3 , plus 115.2 lb. moles H_2 , to 900°C . will be

$$\begin{aligned}\Delta H &= 38.4 \int_{298}^{1173} (19.44 + 7.03 \cdot 10^{-3}T) dT \\ &\quad + 115.2 \int_{298}^{1173} (6.62 + 0.81 \cdot 10^{-3}T) dT. \\ \Delta H &= 38.4(21,540) + 115.2(6,325) \\ &= 1.56 \cdot 10^6 \text{ C.h.u. per ton Cr.}\end{aligned}$$

7. The Effect of Pressure on Enthalpy.—The change of enthalpy with pressure may be computed from the equation (L-R, p. 134)

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = V(1 - \alpha T), \quad (2.18)$$

where α is the coefficient of thermal expansion. For gases under moderate pressure Berthelot's equation may be used in order to integrate this equation. Differentiation of the equation

$$PV = RT \left[1 + \frac{9}{128} \frac{PT_c}{P_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right] \quad (2.19)$$

and substitution in (2.18) yield the following equation for computing the increment in heat content when a gas is subjected to the pressure P ,

$$H_p - H_1 = \frac{9RT_c}{128P_c} \left(1 - 18 \frac{T_c^2}{T^2} \right) (P - 1). \quad (2.20)$$

In this equation, H_1 represents the enthalpy at 1 atm., H_p the enthalpy at the pressure P , and P_c and T_c are the critical constants of the gas in question.

Values computed from Eq. (2.20) should not be treated as more than rough, informative estimates. At high pressures, specific PVT data should be employed in solving (2.18). For example, $H_p - H_1$ may be accurately computed by plotting $V(1 - \alpha T)$ vs. P and measuring the area under the curve so produced between the desired pressure limits.

The change of heat content of liquids with pressure may also be computed from Eq. (2.18). However, owing to the small coefficient of thermal expansion of liquids compared to gases, the effect may usually be neglected, except for liquids near the critical region.

8. The Effect of Pressure on Heat Capacity.—Lewis and Randall (L-R, p. 141) give the following equation for the depend-

ence of C_p on pressure at constant temperature:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P. \quad (2.21)$$

This equation may readily be derived from the definition of C_p and Eq. (2.18). If the gas obeys the ideal gas law in the pressure range of interest, the right-hand side of (2.21) equals zero and the molar-heat capacity is independent of pressure. However, even the so-called "permanent" gases exhibit deviations from the ideal behavior at very high pressures; in this case, an increase in C_p is to be expected. For example, Krase and Mackey⁵ measured the molar-heat capacity at constant pressure of N_2 and found 9.12 cal./deg. at 500 atm. and 30°C., which compares with the value 6.97 at 1 atm. and 30°C. When equation of state data are available for integrating Eq. (2.21), it should be remembered that, if the volume is expressed in liters and the pressure in atmospheres, the heat capacity will be expressed in liter-atmospheres per degree, and may be converted to calories per degree by multiplying by 24.21.

9. The Heat Capacity of Gaseous Carbon Dioxide under Pressure. *Illustration 2.*—The molar-heat capacity of CO_2 , at ordinary pressures, is expressed by the equation

$$C_p = 10.34 + 2.74 \cdot 10^{-3}T - 1.955 \cdot 10^{-5}T^2. \quad (2.22)$$

For heat interchange calculations on a certain process utilizing CO_2 at pressures around 50 atm., an estimate of the increase in heat capacity of the CO_2 would be useful in the temperature range 100 to 300°C.

Solution.—The Berthelot equation of state may be employed with fair accuracy at these pressures in order to solve the problem. Successive differentiation of Eq. (2.19) yields

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{324}{128} \frac{RT_c^3}{P_c T^4}, \quad (2.23)$$

where P_c and T_c are the critical pressure and critical temperature, respectively. Substituting Eq. (2.23) in (2.21) and integrating yield

$$C_p - C_{p_1} = \left(\frac{324}{128} \frac{RT_c^3}{P_c T^3}\right) (P - 1), \quad (2.24)$$

where C_p represents the molar-heat capacity at constant pressure, at the pressure P , and C_{p_1} represents the heat capacity around 1 atm. The heat capacity is practically independent of pressure at about 1 atm. Substituting

$$\begin{array}{ll} T = 373^\circ\text{K.} & P_c = 73 \text{ atm.} \\ T_c = 304.2^\circ\text{K.} & P = 50 \text{ atm.} \end{array}$$

in Eq. (2.24) indicates an increase of 1.83 cal. in the molar-heat capacity, at 100°C. and 50 atm., over the value at ordinary pressures. From Eq. (2.22) C_p , at 100° , equals 9.94; hence the estimated pressure increase corresponds to 18.4 per cent of the ordinary value. The computed increase is probably on the low side.

10. Enthalpy Changes Accompanying Changes in State of Aggregation of Matter.—The correct evaluation of the heat content of a system, under any conditions of temperature and pressure, requires, in addition to data on the heat capacities of the components of the system, a knowledge of the heat effects accompanying vaporization, fusion, and crystallographic transitions, experienced by the system in reaching the state in question. Enthalpy changes accompanying solution and chemical reactions are discussed under separate headings in subsequent chapters.

11. Heats of Vaporization.—A molecule in the liquid state possesses kinetic energy of translation associated with the motion of its center of gravity, plus kinetic energy of rotation about axes at the center of gravity, as well as energy associated with various internal degrees of freedom of the molecule. Owing to their close proximity to each other in the liquid state, molecules also possess considerable potential energy, arising from the action of various types of intermolecular forces—forces that tend to restrict movements of the molecules. This term is obviously a function of distances between centers of molecules and orientations of molecules. When a molecule acquires sufficient kinetic energy of translation to overcome the restraining influences of the intermolecular forces acting at the surface of the liquid, plus the energy required to overcome the pressure of the atmosphere on the liquid, the molecule vaporizes; and the heat absorption involved in the vaporization of 1 mole is called the “heat of vaporization.” The term, heat of vaporization, usually signifies the heat absorbed per mole when the vapor pressure of the liquid

equals 1 atm., *i.e.*, vaporization at the normal boiling point. Very often heats of vaporization at other temperatures and pressures are of interest; in this case, it is necessary to specify the temperature corresponding to the value of the heat of vaporization employed.

Given the heat of vaporization of a liquid at the normal boiling point, the ΔH for any other temperature may readily be computed by means of the equation

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad (2.25)$$

(L-R, p. 102), where ΔH represents the heat effect accompanying the change in state,

$$1 \text{ mole liquid} = 1 \text{ mole vapor.}$$

ΔC_p equals the heat capacity of 1 mole of vapor, minus the heat capacity of 1 mole of liquid. This relation holds at constant pressure. Since the heat capacity in the liquid state is greater than in the gaseous state, ΔC_p is negative; consequently, the heat of vaporization decreases with increasing temperature. For example, the average heat capacity of $\text{H}_2\text{O}(g)$ is about 8.3 cal./deg. from 25 to 100°C.; therefore,

$$\Delta C_p = 8.3 - 18.0 = -9.7 \text{ cal./deg.}$$

for the vaporization of 1 mole of water. Consequently the heat of vaporization at 25° should be about $(9.7)(75) = 727$ cal. greater than ΔH at 100°C. Actually, the molar heat of vaporization of H_2O , at about 25°C., at its saturation vapor pressure, is about 795 cal. greater than the value at 100°C.⁶

Guggenheim⁷ has pointed out that, in order to obtain the temperature coefficients of heats of vaporization, the Kirchhoff equation may not be applied directly, because the process of reversible evaporation at two different temperatures takes place neither between the same volume limits, nor at the same pressure. Thus the correct equation to be employed for calculating the temperature coefficient of heats of vaporization is

$$T \frac{d}{dT} \left(\frac{\Delta H}{T} \right) = \Delta C_{eq}, \quad (2.26)$$

in which heat capacities neither at constant volume nor at constant pressure can be used, but the heat capacities at the saturation vapor pressure, under which the transformation occurs. ΔC_{eq} is, therefore, the difference between the molar-heat capacity at the saturation pressure of the vapor and the corresponding heat capacity of the liquid. The heat capacity of either phase at saturation is related to the usual heat capacity at constant pressure by the equation

$$C_{eq} = C_p - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\Delta H}{\Delta V} \right). \quad (2.27)$$

If the vapor is a perfect gas and the volume of the liquid negligible compared to the vapor volume, Eq. (2.26) reduces to the approximate form (2.25).

A number of empirical rules have been advanced for estimating heats of vaporization. According to Trouton's rule, the molar heat of vaporization at the normal boiling point equals approximately 20.7 times the boiling temperature in degrees Kelvin for a large class of liquids. This rule is quite satisfactory for liquids in which the intermolecular forces are of the simple van der Waals type. Where the energy associated with intermolecular forces is augmented by the presence of dipole-dipole interactions, as in polar liquids, or by the presence of hydrogen bonds, as in liquids containing the OH or NH group, it has been found that the ΔH of vaporization is considerably larger than the value predicted by Trouton's rule. Trouton's constant for water equals 26.0.

Hildebrand has proposed a rule theoretically more sound than Trouton's rule, which states that all liquids of the nonpolar type have practically the same ratio of heat of vaporization to absolute temperature when compared at temperatures where the liquids give the same vapor concentrations. The data in Table 1 illustrate the degree of constancy obtained when the ratio of the heat of vaporization to the temperature at which the vapor concentration equals 0.005 mole/liter is computed.

Data in Table 1 show good constancy of the ratio $\Delta H/T$ for a wide variety of substances, with the exception of ammonia and ethyl alcohol. Both of these substances are quite polar, and, in addition, ethyl alcohol is associated, due to bonds formed through the hydroxyl hydrogen. Although this rule possesses

considerable value from the standpoint of the interpretation of the entropy of vaporization and the prediction of order or lack of order in the arrangement of molecules in the liquid state, it is not convenient for estimating heats of vaporization for ordinary thermochemical purposes. When sufficient vapor-pressure data are available for locating the temperature at which the vapor concentration has some definite value, it is possible and easier to obtain a good estimate for the heat of vaporization from the Clapeyron equation, as described in Chap. V.

TABLE 1

| | $\Delta H/T$ |
|---------------------------|--------------|
| Nitrogen..... | 27.6 |
| Chlorine..... | 27.8 |
| Pentane..... | 27.0 |
| Carbon tetrachloride..... | 27.0 |
| Benzene..... | 27.4 |
| Stannic chloride..... | 27.2 |
| Mercury..... | 26.2 |
| Ammonia..... | 32.0 |
| Ethyl alcohol..... | 33.4 |

A somewhat more accurate relation than Trouton's rule for estimating heats of vaporization of nonpolar liquids at the normal boiling point is the following equation, due to Kistiakowsky:

$$\frac{\Delta H}{T_B} = 8.75 + 4.575 \log T_B. \quad (2.28)$$

12. Heats of Fusion.—A solid substance passes over to the liquid state when it is heated to a temperature such that the vibrational motion of the molecules, atoms, or groups of atoms, constituting the structural units, becomes violent enough to overcome the restraining influences of the crystal forces. The temperature at which the solid phase is in equilibrium with the liquid phase, under a pressure of 1 atm., is called the "melting point" of the substance. The melting point, unlike the boiling point, is not particularly sensitive to moderate pressure changes.

In a rough way, the heat required to melt 1 mole of the substance at its melting point (heat of fusion) is a measure of the magnitude of these crystal forces and the increased number of degrees of freedom or states acquired by the substance on going over to the liquid phase. From the standpoint of the latter item, it is the ratio of the molar heat of fusion to the melting tempera-

ture in degrees absolute—the entropy of fusion—that is more significant than the heat of fusion itself. Consequently some sort of constancy of entropy of fusion might be expected for solids undergoing similar internal processes at the melting point.

Examination of available data on heats of fusion, in conjunction with melting points, discloses the following very rough generalizations:

a. For most elements,

$$\frac{\Delta H}{T_m} = 2 - 3, \quad (2.29)$$

where ΔH equals the molar heat of fusion at the melting point T_m (°K.).

b. For most inorganic compounds,

$$\frac{\Delta H}{T_m} = 5 - 7. \quad (2.30)$$

c. For most organic compounds,

$$\frac{\Delta H}{T_m} = 9 - 11. \quad (2.31)$$

There are many exceptions to the above rules; therefore the rules should be used only after the complete absence of all direct or indirect experimental data has been definitely established. Some outstanding exceptions to these rules are found in the case of N_2O_4 , for which the entropy of fusion is 13.4 units, and HCl and HBr, for which the entropies of fusion are only 3.0 units. In the case of HCl and HBr, the absence of discontinuities in the dielectric constant-temperature curve in the region of the melting point is regarded as proof that the molecules of HCl and HBr are rotating about their centers of gravity in the crystal state. Consequently, since the molecules have already acquired rotational degrees of freedom characteristic of the liquid state, the entropy of fusion is smaller than is to be expected for true solid-liquid transitions. In addition to a number of inorganic substances exhibiting rotation in the solid state, a constantly increasing number of aliphatic and aromatic organic compounds are showing dielectric evidence of rotation in the solid state. In general, rotation appears to be possible in compounds possessing a certain amount of spherical or circular

symmetry, and low heats of fusion are, therefore, to be expected for such compounds.

The temperature coefficient of heat of fusion has been shown by Planck⁷ to be given by the equation

$$\frac{d(\Delta H)}{dT} = \Delta C_p + \frac{\Delta H}{T} - \frac{\Delta H}{T} \left(\frac{\partial \ln \Delta V}{\partial \ln T} \right)_P. \quad (2.32)$$

Since the last term on the right side is usually small,

$$\frac{d(\Delta H)}{dT} = \Delta C_p + \frac{\Delta H}{T}. \quad (2.33)$$

13. Heats of Transition.—Many substances, when heated, have been found to exhibit regions of isothermal, or substantially isothermal, heat absorption without undergoing melting or vaporizing. The heat absorption is believed to be due to a change in the crystal lattice or the onset of rotation in the crystal. The heat absorbed per mole is called the “molar heat of transition.” Some substances exhibit a series of such transitions—the form stable at the lowest temperature being designated by α , the next highest, β , etc. No generalizations can be formulated for estimating heats of transition, and, indeed, the existence and temperature of a transition are entirely matters of experimental knowledge. When the observed entropy of fusion is low, as in the case of HCl, a transition might be expected such that the entropy of transition, plus fusion, would add up to the more or less normal value of 5–7 units. In the case of HCl, the onset of rotation is indicated by a transition at 98.4°K., with a heat absorption of 284.3 cal. Thus, the transition entropy change is 2.89 units, and the total transition, plus fusion entropy, is 5.89 units, in agreement with the above rough generalization for inorganic compounds. The estimation of heats of transition is hazardous; but, since they are usually small, their importance in most thermochemical considerations is correspondingly small. The temperature coefficient of heats of transition may be calculated by means of Eq. (2.33).

The foregoing brief discussion of methods for computing enthalpy changes in physical changes of state—with the exception of solution—permits the evaluation of the enthalpy of a system at any desired temperature, pressure, or state, provided that no chemical interaction has occurred. Since absolute

values of heat contents cannot be evaluated, but only the increase in heat content above an arbitrarily chosen zero level, it is essential that an unambiguous statement of this level be made. As a general rule, the zero level is 0°C. and that form of the substance which is stable at 0° . There are numerous exceptions to this choice, but as long as the conditions are definitely stated, data can be converted from one system to another by means of a small additive correction term. Tabulations of water enthalpies use liquid water at 0°C. , under its own vapor pressure, as a base level. Water, under 1 atm. pressure, at 0°C. , possesses 0.441 international steam table calorie of enthalpy per mole when referred to this datum.

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CHAPTER III

THERMAL EFFECTS ACCOMPANYING SOLUTION PROCESSES

1. Integral and Partial Molar Heats of Solution.—The chemist or chemical engineer, dealing with the heat changes accompanying processes of solution or the reverse, is apt to be confronted with one or both of two major types of problems. An example of the first kind would be the computation of the total heat generated by a given solution process in order that an estimate may be made of the heat interchange surface required to keep the temperature of the system within certain preassigned limits. For example, the problem might be the estimation of the cooling requirements for the production of dilute hydrochloric acid by burning hydrogen and chlorine, followed by absorption of the cooled hydrogen chloride gas in water. Obviously, the first step in the solution of such a problem would be the calculation of the total heat generated per unit of HCl by the absorption of gaseous HCl in enough water to form a solution of the desired concentration.

Again, it might be of interest to compute the total heat required to concentrate the dilute solution of sodium hydroxide, produced by the electrolysis of sodium chloride brines, up to, say, a 50 per cent solution. Although this is the reverse of the hydrochloric acid example, one of the items required is a knowledge of the heat liberated when the necessary amounts of water and salt are added to a 50 per cent solution to produce the original dilute solution. The heats of solution involved in considerations of this kind are known as total or integral heats of solution or dilution.

The second type of heat effect involved in processes of solution is that which determines the temperature coefficient of the free-energy changes accompanying the reversible, isothermal transfer of the components of a solution between solutions of two different concentrations. By means of standard thermodynamic relations it is possible to compute the free-energy changes accompanying

these transfer processes under isothermal conditions. Since the derivation of these free-energy relations requires constancy of composition of the initial and final states during the process of transfer, it is obvious that the corresponding heat effect must also correspond to the heat absorption accompanying the transfer performed under the same conditions; hence the need for partial molar heats of solution.

That is, the partial molar heat of solution of any given component of a solution, at a definite concentration, is defined as the quantity of heat absorbed per mole of substance when dissolved under conditions such that the composition of the solution does not change appreciably. The direct measurement of this quantity may be effected, either by measuring the heat absorbed when a very small but definite amount of substance is dissolved in a moderate quantity of solution, or by measuring the heat effect accompanying the addition of a moderate amount of the substance to a very large quantity of solution. Because the nomenclature and symbols employed in the thermochemistry of solutions are quite elaborate, it would appear that the most effective method of presenting the subject would be by means of a definite illustrative problem.

2. Partial Molar-heat Capacities and Heat Contents in Hydrochloric Acid Solutions. *Illustration.*—The absorption of gaseous hydrogen chloride at about atmospheric pressure, in water or dilute hydrochloric acid, may be used to produce acid approaching a concentration of about 30 weight per cent. The heat generated in the process is considerable; and a knowledge of heat capacities and heats of solution is of fundamental importance in the computation of adiabatic temperature rises, cooling water and heat interchange surface requirements, etc. A summary of available data on heat capacities and heat contents of hydrochloric acid solutions, over as wide a range of concentrations as possible, is therefore of firsthand importance as a basis for engineering design considerations. The information required is as follows:

a. Heat Capacities:

1. The apparent molar-heat capacities of the HCl: Φ .
2. The partial molar-heat capacities of the HCl: \bar{C}_{p_2} .
3. The relative partial molar-heat capacities of the H_2O :
 $\bar{C}_{p_1} - \bar{C}_{p_1}^\circ$.

b. Heats of Solution:

1. The relative apparent molar-heat contents of the HCl:
 $\Phi_h - \Phi_h^\circ$.
2. The relative partial molar-heat contents of the HCl:
 $\bar{H}_2 - \bar{H}_2^\circ$.
3. The relative partial molar-heat contents of the H₂O:
 $\bar{H}_1 - \bar{H}_1^\circ$.

Solution.—The available data on heat capacities and heat contents of hydrochloric acid solutions are summarized in four papers by Rossini.¹⁻⁴ (See also Sturtevant.⁵)

a. Heat Capacities.—Concentrations of aqueous solutions are usually expressed in terms of the molality m , which equals the moles of solute per kilogram of H₂O. Accordingly, Eqs. (2.15) and (2.16) become

$$C_p = n_1 \bar{C}_{p_1} + m \bar{C}_{p_2} = 55.51 \bar{C}_{p_1} + m \bar{C}_{p_2}, \quad (3.1)$$

where $\bar{C}_{p_1} = \frac{\partial C_p}{\partial n_1}$, and $\bar{C}_{p_2} = \frac{\partial C_p}{\partial m}$.

In this equation, C_p represents the heat capacity of 1 kg. H₂O, plus m moles of solute; and \bar{C}_{p_1} and \bar{C}_{p_2} are the partial molar-heat capacities of H₂O and HCl, respectively.

A convenient quantity when dealing with the heat capacities of aqueous solutions is the apparent molar-heat capacity of the solute Φ_c , which is defined by means of the equation

$$\Phi_c = \frac{C_p - 55.51 \bar{C}_{p_1}^\circ}{m}. \quad (3.2)$$

Thus it can be seen that Φ_c would be the contribution of 1 mole of solute to the heat capacity of the solution, if the contribution of the H₂O were the same as that of pure water. In other words, $m\Phi_c$ is the difference between the total heat capacity of the solution containing m moles of solute and the heat capacity of 1,000 g. water; it may be positive or negative. When tabulations of Φ_c vs. molality are available, the actual heat capacity per gram of solution (specific heat) may be computed from the relation

$$c = \frac{m\Phi_c + 1,000}{mM + 1,000}, \quad (3.3)$$

where M is the molecular weight of the solute.

A relatively simple method for computing Φ_c , \bar{C}_{p2} , and $\bar{C}_{p1} - \bar{C}_{p1}^\circ$ from measurements of total heat capacities has been devised by Randall and Rossini.⁶ Rewriting Eq. (3.2) and differentiating yield

$$\bar{C}_{p2} = \frac{dC_p}{dm} = m \frac{d\Phi_c}{dm} + \Phi_c. \quad (3.4)$$

Substituting $dm = 2m^{1/2}d(m^{1/2})$ in Eq. (3.4) yields

$$\bar{C}_{p2} = \frac{m^{1/2}}{2} \frac{d\Phi_c}{d(m^{1/2})} + \Phi_c. \quad (3.5)$$

Thus the slope of the plot of Φ_c vs. $m^{1/2}$ multiplied by $m^{1/2}/2$ and added to the corresponding value of Φ_c is equal to the partial molar-heat capacity of the solute at that molality. It will be noted that a plot of Φ_c vs. $m^{1/2}$ instead of m has been used to evaluate \bar{C}_{p2} . This is due to the fact that the curvature of most thermodynamic functions when plotted against the square root of the molality is considerably reduced; in the case of apparent molar-heat capacities a practically straight line is obtained, which may readily be extrapolated to infinite dilution.

Elimination of C_p from Eqs. (3.1) and (3.2) and substitution of the value of \bar{C}_{p2} , given by Eq. (3.5), yield the following equation for computing the relative partial molar-heat content of the water in the solution of molality m :

$$\bar{C}_{p1} - \bar{C}_{p1}^\circ = \frac{-m}{55.51} \left[\frac{m^{1/2}}{2} \frac{d\Phi_c}{d(m^{1/2})} \right]. \quad (3.6)$$

Equations (3.2), (3.5), and (3.6) constitute the necessary tools for computing the three basically important heat capacities of aqueous solutions, starting with measurements of the total heat capacity C_p .

A careful review of the existing data on HCl and other numerous strong electrolytes has led Rossini to conclude that the apparent heat capacity of the solute may be expressed as a linear function of $m^{1/2}$ within the experimental accuracy, in accordance with an equation of the form

$$\Phi_c = \Phi_c^\circ + Am^{1/2}, \quad (3.7)$$

where Φ_c° equals the apparent partial molar-heat capacity of the solute at infinite dilution, which is the same thing as the partial

molar-heat capacity of the solute at infinite dilution $\bar{C}_{p_1}^\circ$. Substitution of Eq. (3.7) in (3.5) and (3.6) gives the equations

$$\bar{C}_{p_2} = \bar{C}_{p_2}^\circ + \frac{3}{2}Am^{1/2}, \quad (3.8)$$

$$\bar{C}_{p_1} - \bar{C}_{p_1}^\circ = -\frac{A}{2(55.51)}(m^{3/2}). \quad (3.9)$$

Examination of Eqs. (3.7) to (3.9) indicates that, provided the $m^{1/2}$ relation holds over the concentration range of interest, it is necessary to make only two reliable measurements of the heat capacity to determine the two constants, $\bar{C}_{p_2}^\circ$ and A , of the foregoing set of equations, in order to obtain a complete set of heat-capacity data. It is interesting to note that the partial molar-heat capacity of the solute is a function of $m^{1/2}$, whereas the relative partial molar-heat capacity of the solvent is a function of $m^{3/2}$.

The result of a critical study of the data on hydrochloric acid solutions has led Rossini⁴ to deduce the values, -32.5 and 7.2 , for the two constants, $\bar{C}_{p_2}^\circ$ and A , respectively. Thus, Eqs. (3.7) to (3.9) for hydrochloric acid, in the range of concentrations from 0 to 16 molal (36.8 per cent), at 25°C ., become

$$\Phi_c = -32.5 + 7.2m^{1/2}, \quad (3.10)$$

$$\bar{C}_{p_2} = -32.5 + 10.8m^{1/2}, \quad (3.11)$$

$$\bar{C}_{p_1} - \bar{C}_{p_1}^\circ = -0.065m^{3/2}. \quad (3.12)$$

Heat capacities computed from these equations are in calories per degree centigrade per mole. Approximate values for the temperature coefficients of these quantities, in the temperature range from 10 to 35°C ., are

$$\frac{d\Phi_c}{dT} = \frac{d\bar{C}_{p_2}}{dT} = 0.285, \quad (3.13)$$

$$\frac{d(\bar{C}_{p_1} - \bar{C}_{p_1}^\circ)}{dT} = 0. \quad (3.14)$$

Equations (3.10) to (3.14) represent the desired correlation of the available data on the heat capacities of aqueous solutions of hydrochloric acid.

The method of handling the following experimental data in order to obtain Eqs. (3.10) to (3.12) is given below. Observed heat capacities (C_p) represent the heat capacities of the system containing m moles of solute in 55.51 moles H_2O .

Temperature = 25°C.

| | | | | | |
|-------------|---------|--------|--------|---------|--------|
| m | 0.10 | 0.50 | 1.00 | 1.50 | 2.00 |
| C_p | 996.965 | 986.02 | 974.31 | 964.045 | 954.98 |

Values of the apparent molar-heat capacity (Φ_c) of the HCl are first computed from the above values of C_p and Eq. (3.2). These values are then plotted against the square root of the molality and, as shown on Fig. 1, a straight line is obtained with an

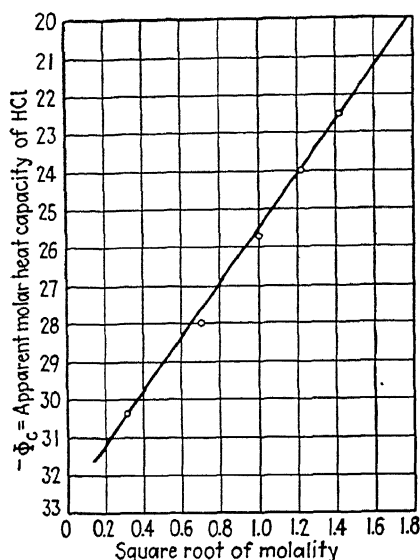


FIG. 1.—Apparent molar-heat capacities of HCl in aqueous solutions at 25°C.

intercept on the y -axis equal to -32.5 . This corresponds to the partial molar-heat capacity of the HCl at infinite dilution $\bar{C}_{p_1}^\circ$. The slope of the curve $d\Phi_c/d(m^{1/2})$ may readily be found to be equal to $7.2(A)$ from this plot, and, accordingly, values of \bar{C}_{p_2} for the different molalities are computed from Eq. (3.5); corresponding values of $\bar{C}_{p_1} - \bar{C}_{p_1}^\circ$ are computed from Eq. (3.6). Computed values of Φ_c , \bar{C}_{p_2} , and $\bar{C}_{p_1} - \bar{C}_{p_1}^\circ$, corresponding to the above values of C_p , are recorded in Table 1. Equations (3.10) to (3.12) are readily set up by using the graphically determined values of $\bar{C}_{p_1}^\circ$ and A .

TABLE 1.—HEAT CAPACITIES IN DILUTE AQUEOUS HCl SOLUTIONS AT 25°C.
[Cal./(mole)(deg. C.)]

| <i>m</i> , moles HCl per kilogram H ₂ O | <i>m</i> ^{1/2} | <i>C_p</i> , cal. per (55.51 + <i>m</i>) moles solution | Φ _c | \bar{C}_{p_2} | $\bar{C}_{p_1} - \bar{C}_{p_1}^{\circ}$ |
|--|-------------------------|---|----------------|-----------------|---|
| 0.10 | 0.316 | 996.965 | -30.35 | -29.21 | -0.00203 |
| 0.50 | 0.707 | 986.020 | -27.96 | -25.41 | -0.0229 |
| 1.00 | 1.000 | 974.310 | -25.69 | -22.09 | -0.0648 |
| 1.50 | 1.225 | 964.045 | -23.97 | -19.56 | -0.119 |
| 2.00 | 1.414 | 954.980 | -22.51 | -17.41 | -0.183 |

b. Heats of Solution.—Just as the heat capacity of a pure substance at constant pressure is defined by means of the equation

$$C_p = \frac{dH}{dT},$$

so the partial molar-heat capacity of any given component of a solution is defined by means of the equation

$$\bar{C}_{p_i} = \frac{d\bar{H}_i}{dT},$$

where the partial molar-heat content is defined by the equation

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i} \right)_{n, P, T}. \quad (3.15)$$

The partial molar-heat content of each component of the solution is defined analogously to the partial molar-heat capacity. That is, \bar{H}_i represents the increase in heat content of the solution per mole of the *i*th component, accompanying the addition of an infinitesimal quantity of *i* to the solution—all other variables remaining constant. The total heat content of a binary solution is, therefore,

$$H = n_1\bar{H}_1 + n_2\bar{H}_2, \quad (3.16)$$

or, in the case of aqueous solutions with concentrations expressed in terms of molalities,

$$H = 55.51\bar{H}_1 + m\bar{H}_2. \quad (3.17)$$

The apparent molar-heat content of the solute is defined by an equation analogous to Eq. (3.2); thus,

$$\Phi_h = \frac{H - 55.51\bar{H}_1^\circ}{m}, \quad (3.18)$$

where \bar{H}_1° equals the partial molar-heat content of the water in the infinitely dilute solution. That is, the apparent molar-heat content of the solute would be the contribution of 1 mole of solute to the heat content of the solution if the contribution of the water were the same as that of the pure water. At infinite dilution the apparent molar-heat content of the solute becomes equal to the true partial molar-heat content of the solute; hence

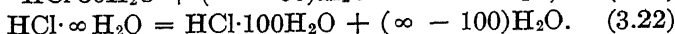
$$\Phi_h^\circ = \bar{H}_2^\circ. \quad (3.19)$$

In the compilations of heats of formation of substances in aqueous solutions given in I.C.T., Vol. 5, and Bichowsky and Rossini,⁷ concentrations are usually expressed as moles of H_2O per mole of solute; that is, the expression $\text{HCl}\cdot 100\text{H}_2\text{O}$ signifies a solution containing 1 mole of $\text{HCl}/100$ moles H_2O , which is equal to a molality of 0.555. The reader should, therefore, become accustomed to using heats of solution data in both forms.

As a starting point for the evaluation of heat of solution data, suppose it is desired to compute the change in enthalpy or heat absorbed when a solution of concentration, say, $\text{HCl}\cdot 50\text{H}_2\text{O}$, is diluted down to a concentration, $\text{HCl}\cdot 100\text{H}_2\text{O}$. The change of state involved may be expressed by means of the equation



If we consider the processes represented by the two following equations, it is obvious that the sum of these two equations is equal to the process expressed by Eq. (3.20):



Thus, if the total heats absorbed when the solutions $\text{HCl}\cdot 50\text{H}_2\text{O}$ and $\text{HCl}\cdot 100\text{H}_2\text{O}$ are diluted down to infinite dilution are known, the enthalpy change corresponding to Eq. (3.20) may be computed from the relation

$$\Delta H_{100-50} = \Delta H_{\infty-50} - \Delta H_{\infty-100},$$

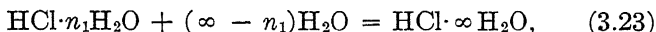
where ΔH_{100-50} and $\Delta H_{\infty-50}$ represent the heat changes accompanying reactions (3.20) and (3.21), as written, and $\Delta H_{\infty-100}$ is the heat change accompanying the reverse of (3.22). Similarly, the ΔH accompanying the dilution of $\text{HCl} \cdot 100\text{H}_2\text{O}$ down to $\text{HCl} \cdot 500\text{H}_2\text{O}$ may be computed from the relation

$$\Delta H_{500-100} = \Delta H_{\infty-100} - \Delta H_{\infty-500}.$$

It may, therefore, be seen that, if the total heat effect accompanying the dilution of solutions of definite concentrations down to infinite dilution is known, it is a relatively simple process to compute the heats of dilution between any other pairs of concentrations of possible interest.

It is also possible, as the following development will show, to compute the partial molar heats of solution necessary for dealing with the reversible, isothermal transfer of matter between solutions of different concentrations.

The ΔH corresponding to the process,



is

$$\Delta H = \bar{H}_2^\circ + \infty \bar{H}_1^\circ - (\infty \bar{H}_1^\circ - n_1 \bar{H}_1^\circ + \bar{H}_2 + n_1 \bar{H}_1), \quad (3.24)$$

or

$$\Delta H = \bar{H}_2^\circ - \bar{H}_2 + n_1(\bar{H}_1^\circ - \bar{H}_1). \quad (3.25)$$

In terms of the apparent molar-heat content of the HCl [Eq. (3.18)] the heat content of the right-hand side of Eq. (3.23) is given by the expression $\Phi_h^\circ + \infty \bar{H}_1^\circ$, and the heat content of the left side by $\Phi_h + \infty \bar{H}_1^\circ$. Hence, the difference, ΔH , is simply

$$\Delta H = \Phi_h^\circ - \Phi_h, \quad (3.26)$$

where Φ_h° is the apparent molar-heat content of the solute at infinite dilution, which is equal to the partial molar-heat content \bar{H}_2° of the HCl at infinite dilution. Equation (3.26) illustrates the convenience of apparent molar-heat contents, since the enthalpy change per mole of solute accompanying dilution is exactly the difference between the apparent molar-heat contents at the two concentrations involved. Differences of apparent molar-heat contents are obtained directly from calorimetric measurements, as indicated by Eq. (3.26), and the partial molar-heat contents of the individual components are computed

from these quantities. Equating Eqs. (3.25) and (3.26) yields

$$-\Delta H = \Phi_h - \Phi_h^\circ = \bar{H}_2 - \bar{H}_2^\circ + n_1(\bar{H}_1 - \bar{H}_1^\circ). \quad (3.27)$$

The differences $\bar{H}_1 - \bar{H}_1^\circ$ and $\bar{H}_2 - \bar{H}_2^\circ$ have been called the "relative" heat contents of the solvent and solute, respectively, by Lewis and Randall, and designated by the symbols L_1 and L_2 . However, in order to minimize the number of new symbols, the use of ordinary partial molar-heat contents will be adhered to.

The method employed by Rossini for extrapolating heats of dilution obtained between finite concentrations down to infinite dilution and the procedure employed for deriving partial molar-heat contents are described by Rossini.² Briefly, the procedure is as follows: Rewriting Eq. (3.27) and expressing concentrations in terms of molalities give for the heat change, corresponding to m moles of solute,

$$-\Delta H = m(\Phi_h - \Phi_h^\circ) = m(\bar{H}_2 - \bar{H}_2^\circ) + 55.51(\bar{H}_1 - \bar{H}_1^\circ). \quad (3.28)$$

Differentiation of Eq. (3.28) with respect to m yields

$$m \frac{d(\Phi_h - \Phi_h^\circ)}{dm} + \Phi_h - \Phi_h^\circ = \bar{H}_2 - \bar{H}_2^\circ + m \frac{d(\bar{H}_2 - \bar{H}_2^\circ)}{dm} + 55.51 \frac{d(\bar{H}_1 - \bar{H}_1^\circ)}{dm}. \quad (3.29)$$

From the fundamental equation of partial molar quantities in the form (L-R, p. 43),

$$\sum n_i d\bar{G}_i = 0, \quad (3.30)$$

where \bar{G}_i is any partial molar property of the i th component, and n_i is the corresponding number of moles, it follows that the sum of the last two terms on the right-hand side of Eq. (3.29) equals zero. Hence,

$$\bar{H}_2 - \bar{H}_2^\circ = \Phi_h - \Phi_h^\circ + m \frac{d(\Phi_h - \Phi_h^\circ)}{dm}. \quad (3.31)$$

Substitution of $dm = 2m^{1/2}d(m^{1/2})$ gives

$$\bar{H}_2 - \bar{H}_2^\circ = \Phi_h - \Phi_h^\circ + \frac{m^{1/2}}{2} \frac{d(\Phi_h - \Phi_h^\circ)}{d(m^{1/2})}. \quad (3.32)$$

Eliminating $\bar{H}_2 - \bar{H}_2^\circ$ from this equation by substituting its value from Eq. (3.28) gives the desired relation for computing $\bar{H}_1 - \bar{H}_1^\circ$,

$$\bar{H}_1 - \bar{H}_1^\circ = \frac{-m}{55.51} \left[\frac{m^{1/2}}{2} \frac{d(\Phi_h - \Phi_h^\circ)}{d(m^{1/2})} \right]. \quad (3.33)$$

The procedure for computing the various heat-content data is indicated by Eqs. (3.32) and (3.33). When the values of $\Phi_h - \Phi_h^\circ$ have been obtained by proper extrapolation of measured heats of dilution, these values are plotted against the square root of the molality in order to reduce the curvature of the plot. The relative partial molar-heat content of the solute $\bar{H}_2 - \bar{H}_2^\circ$ is then computed by measuring the slope of this plot at the desired molality and by performing the arithmetical operations required by Eq. (3.32). Similarly, values for the relative partial molar-heat content of the water may be computed from Eq. (3.33) and the already measured slopes of the $(\Phi_h - \Phi_h^\circ) - m^{1/2}$ plot.

Rossini⁴ gives the following values for the experimentally determined relative apparent molar-heat content of HCl in aqueous solutions at 25°C.:

| Composition | $\Phi_h - \Phi_h^\circ$, g. cal. per mole HCl |
|---------------------------|---|
| HCl-1,600H ₂ O | 90 |
| HCl-400H ₂ O | 181 |
| HCl-200H ₂ O | 249 |
| HCl-100H ₂ O | 343 |
| HCl-50H ₂ O | 483 |
| HCl-25H ₂ O | 730 |
| HCl-20H ₂ O | 850 |
| HCl-15H ₂ O | 1,050 |
| HCl-12H ₂ O | 1,250 |
| HCl-10H ₂ O | 1,460 |
| HCl-5H ₂ O | 2,760 |
| HCl-3H ₂ O | 4,470 |

These data have been plotted against $m^{1/2}$ on Fig. 2, and graphically determined slopes have been used to compute the values of $\bar{H}_2 - \bar{H}_2^\circ$ and $\bar{H}_1 - \bar{H}_1^\circ$ recorded in Table 2.

Examination of the derived data contained in Table 2 discloses the interesting fact that, even in the most dilute solution recorded (0.035*m*), the deviation of the partial molar-heat content of the HCl from its value in the infinitely dilute solution (−39,943 cal.) exceeds 0.3 per cent; whereas the H₂O partial molar-heat content

in a 4.63 molal solution deviates by less than 0.2 per cent from its value in the infinitely dilute solution. Thus, for most thermochemical calculations involving the heat of formation of H_2O in dilute hydrochloric acid solution, no great error would be introduced by using the value for pure water. The fact that the relative apparent molar-heat contents are positive over the entire

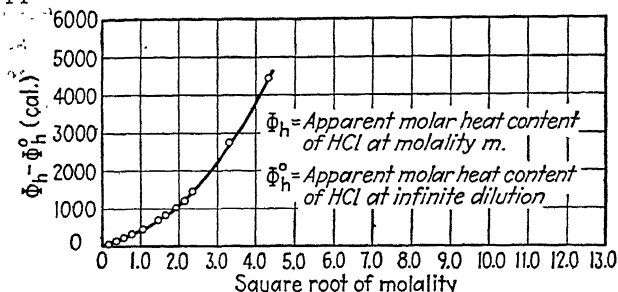


FIG. 2.—Apparent molar-heat contents of HCl in aqueous solutions at 25°C.

range of concentrations shows that addition of water to any concentration of acid results in the liberation of heat. For example, dilution of a solution containing 1 mole of HCl in 20 moles of H_2O with an infinite quantity of water at 25°C. results in the liberation of 850 cal. of heat.

TABLE 2.—APPARENT AND PARTIAL MOLAR-HEAT CONTENTS IN HYDROCHLORIC ACID SOLUTIONS AT 25°C.
(cal/mole)

| Concentration | m , moles HCl per kg. H_2O | $m^{1/2}$ | $\Phi_h - \Phi_h^\circ$ | $\frac{d(\Phi_h - \Phi_h^\circ)^*}{dm^{1/2}}$ | $H_2 - H_2^\circ$ | $H_1 - H_1^\circ$ |
|--------------------------------|--|-----------|-------------------------|---|-------------------|-------------------|
| HCl-1,600 H_2O | 0.0347 | 0.186 | 90 | 435 | 131 | -0.0253 |
| HCl-400 H_2O | 0.140 | 0.374 | 181 | 435 | 262 | -0.205 |
| HCl-200 H_2O | 0.278 | 0.527 | 249 | 435 | 364 | -0.575 |
| HCl-100 H_2O | 0.555 | 0.745 | 343 | 435 | 505 | -1.62 |
| HCl-50 H_2O | 1.110 | 1.054 | 483 | 545 | 771 | -5.76 |
| HCl-25 H_2O | 2.220 | 1.490 | 730 | 545 | 1,136 | -16.3 |
| HCl-20 H_2O | 2.776 | 1.666 | 850 | 730 | 1,459 | -30.4 |
| HCl-15 H_2O | 3.701 | 1.924 | 1,050 | 748 | 1,770 | -48.0 |
| HCl-12 H_2O | 4.626 | 2.150 | 1,250 | 990 | 2,315 | -88.8 |
| HCl-10 H_2O | 5.551 | 2.356 | 1,460 | 1,010 | 2,650 | -119.0 |
| HCl-5 H_2O | 11.10 | 3.320 | 2,760 | 1,700 | 5,580 | -564.0 |
| HCl-3 H_2O | 18.50 | 4.300 | 4,480 | 1,900 | 8,570 | -1,362.0 |

* See Fig. 2 for values of $d(\Phi_h - \Phi_h^\circ)/dm^{1/2}$.

For certain calculations the value of the partial molar-heat content of the solute \bar{H}_2 , rather than the relative partial molar-heat content, is required. In order to compute values of \bar{H}_2 it is necessary to determine the value of \bar{H}_2° , the heat of formation of the HCl in the infinitely dilute solution from its elements in their standard states, at constant pressure. Since the heat of formation of gaseous HCl from the elements is a well-known datum, it is necessary to know only the heat of solution of HCl. That is, the enthalpy change corresponding to the reaction



where *aq* indicates the infinitely dilute solution. Rossini⁴ has extrapolated the results of several sets of measurements of the heat effect accompanying the process,



down to infinite dilution and obtained the value

$$\Delta H_{298.1} = -17,880 \text{ cal./mole}$$

for the heat of solution (3.34) of gaseous HCl at 1 atm. Since the standard heat of formation of gaseous HCl from the elements at 25°C. and 1 atm. equals -22,063 cal., the standard heat of formation of 1 mole of HCl in the infinitely dilute solution equals -17,880 + (-22,063) or -39,943 cal. From the values of $\bar{H}_2 - \bar{H}_2^\circ$, recorded in Table 2, the partial molar-heat contents of the HCl, at various concentrations referred to the conventional reference state, may then be computed. For example, $\bar{H}_2 - \bar{H}_2^\circ$ equals 5,580 cal. in HCl·5H₂O; hence

$$\bar{H}_2 = 5,580 - 39,943 = -34,363 \text{ g. cal./mole.}$$

It is important to note that tabulated values for the heats of formation of various substances at different concentrations in aqueous solutions correspond to $-\Phi_h$ values. Thus, in Bichowsky and Rossini (B-R, p. 23), the value Q_f for HCl at 18°C. in HCl·5H₂O is given as 37,100 cal. From Table 2, a value of $\Phi_h - \Phi_h^\circ$ equal to 2,760 is obtained for this concentration; since $\Phi_h^\circ = \bar{H}_2^\circ = -39,943$, this gives $-\Phi_h = 37,183$ cal. at 25°C. The values of Q_f for various substances in aqueous solutions recorded in Bichowsky and Rossini may be used to compute the

corresponding values of the relative partial molar-heat contents of the solute and water, by the technique described above. For example (B-R, p. 138), the values of Q_f for $\text{NaCl} \cdot \infty \text{H}_2\text{O}$ and $\text{NaCl} \cdot 25\text{H}_2\text{O}$ are given as 97,166 and 97,496 cal., respectively, at 18°C . The difference, -330 cal., corresponds to $\Phi_h - \Phi_h^\circ$; accordingly, this gives one point on the plot of $\Phi_h - \Phi_h^\circ$ vs. $m^{1/2}$ used to evaluate $\bar{H}_2 - \bar{H}_2^\circ$ and $\bar{H}_1 - \bar{H}_1^\circ$. Similarly (B-R, p. 33), the values of Q_f for $\text{HNO}_3 \cdot \infty \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 25\text{H}_2\text{O}$ are given as 49,190 and 49,162 cal., respectively, from which $\Phi_h - \Phi_h^\circ$ is found to be 28 cal.

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CHAPTER IV

THERMAL EFFECTS ACCOMPANYING CHEMICAL CHANGES

1. Heats of Formation.—In the three preceding chapters a brief outline has been presented of the more or less conventional procedures employed for evaluating changes of enthalpy and internal energy accompanying physical changes of state. The present chapter is concerned with the methods used in evaluating changes of enthalpy or heat content accompanying chemical reaction—the most important phase of the science of thermochemistry. That is, the principal object of modern theoretical and experimental thermochemistry is the derivation of the necessary data for obtaining heats of formation of all known substances, in addition to such auxiliary data as are required for computing the variation of heats of formation with temperature. Given the heats of formation of all known substances and their entropies of formation, we can then compute the corresponding free energies of formation and consequently the free-energy change and equilibrium constant for any desired chemical reaction.

Since only changes in heat content and not absolute values are measurable in an unambiguous sense, it is necessary to select a common standard temperature for all substances and a standard state for each substance in order to define clearly the significance of the recorded heats of formation. Accordingly, the heat of formation (ΔH) of a given substance represents the increase in heat content, or enthalpy, accompanying the formation of 1 mole of the substance from its elements in their standard states, at a constant pressure of 1 atm. The standard reference state for each element is that form which is most stable at room temperature and 1 atm. pressure. The precise statement of the reference state for gases is that hypothetical standard state of unit fugacity where the heat content of the gas is independent of pressure, *i.e.*, zero pressure for real gases. Since the heat content

of most gases at room temperature and 1 atm. is practically the same as at zero pressure, the distinction is not important.

Present calorimetric practice is to refer the results of all thermochemical investigations to 25°C. as standard temperature, but a great volume of earlier thermochemical data exists which has been referred to 18°C. as the standard. For most purposes the effect of 7 deg. difference of temperature on heats of formation is unimportant; where more precise data are required, it is usually possible to make a good, rapid estimate of the correction from known or estimated heat capacities of the substances involved.

2. Principle of Modern Calorimetry.—In a few instances, as in the case of gaseous HCl, H₂O, and CO₂, it is possible to obtain the heat of formation of a compound by measuring the heat of synthesis directly from its elements. In most cases, however, it is necessary to measure the heat of some reaction in which the heats of formation of all the other reactants and products are known, except that of the desired substance. The heats of formation of most organic compounds have been obtained by measuring the heat evolved when the substance is burned in O₂ under pressure in a bomb of definite volume. In the case of HCl, just above, it is possible to measure the heat of formation from H₂ and Cl₂ at a constant pressure of about 1 atm.; hence, except for minor corrections, the observed heat effect is directly the ΔH of formation. On the other hand, the observations on the combustion reactions in a constant volume bomb under pressure give the energy change corresponding to that pressure, and must be subjected to an elaborate correction technique¹ in order to obtain the corresponding ΔH at 1 atm. and room temperature. Furthermore, the computation of heats of formation from heats of combustion requires a knowledge of the heats of formation of H₂O, CO₂, and other compounds formed in the bomb; consequently, unless these thermochemical constants are known with a high degree of precision, the final accuracy of the computed heat of formation is apt to be low. The reliability of any thermochemical datum is greatly dependent on the analytical procedures employed to establish the products of the reactions and the amounts of the various products formed.

Most of the reactions chosen for thermochemical study are those in which heat is evolved; and the calorimetric method

employed for measuring this heat is, in principle, quite simple.² In brief, the problem consists in determining the quantitative correspondence between the thermal energy liberated by (1) the reaction under investigation and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator. For example, when H_2 and Cl_2 were burned in a constant-pressure calorimeter at substantially 1 atm. pressure at an average temperature of $30^\circ C.$, it was found³ that the formation of 0.1527 mole of HCl was accompanied by a rise in temperature of $0.9116^\circ C.$ In the same apparatus and under substantially identical conditions of temperature and rate of heat generation, it was found that the expenditure of 15,418 international joules of electrical energy was equivalent to a temperature rise of $1^\circ C.$ Consequently, the heat of formation of 1 mole of HCl at $30^\circ C.$ and 1 atm., as determined by this experiment is, except for certain minor corrections,

$$-\Delta H = \frac{(0.9116)(15,418)}{(0.1527)(4.183)} = 22,000 \text{ cal./mole.} \quad (4.1)$$

This substitution method eliminates many of the systematic errors and uncertainties due to heat leakage from the calorimetric system because of their cancellation in the electrical and chemical experiments performed under substantially identical conditions. In the case of endothermic reactions, where heat energy is absorbed, the comparison of the chemical with the electrical energy can be made simultaneously instead of in two separate experiments. That is, the temperature of the calorimeter is maintained practically constant during the course of the chemical reaction by supplying measured electrical energy at the same rate as the reaction absorbs energy.

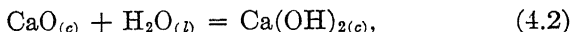
In some instances it may not be convenient to calibrate the calorimetric system by the electrical method; in which case the energy of the unknown reaction is compared under identical conditions with the energy evolution of some "standard" chemical reaction, which has been previously calibrated against electrical energy under these conditions. One of the most commonly used comparison reactions for measuring the energy of bomb reactions is the combustion of highly purified benzoic acid. For example, the heat of combustion of benzoic acid is known

to be⁴ 26,414 international joules per gram (weight *in vacuo*) when the sample is burned under the following standard conditions:

| | |
|---|---------|
| Temperature to which reaction is referred..... | 30°C. |
| Initial O ₂ pressure in bomb at 30°C..... | 30 atm. |
| Mass of water placed in bomb per liter of bomb volume | 3 g. |
| Mass of benzoic acid burned per liter of bomb volume | 3 g. |

3. Calculation of ΔH of Formation from ΔH of Reaction.

Illustration 1.—The ΔH of reaction



as given by three different investigators, is $-15,300$, $-15,180$, and $-15,300$ cal. (B-R, p. 344) at 18°C . Compute the standard heat of formation of $\text{Ca}(\text{OH})_2$ at this temperature.

Solution.—The average ΔH for reaction (4.2) is $-15,260$, and Bichowsky and Rossini give $-68,370$ and $-151,800$ cal. for the heats of formation of liquid H_2O and CaO , respectively. The ΔH of the above reaction is

$$\Delta H = -15,260 = \Delta H_{\text{Ca}(\text{OH})_2} - \Delta H_{\text{CaO}} - \Delta H_{\text{H}_2\text{O}}. \quad (4.3)$$

Therefore,

$$\Delta H_{\text{Ca}(\text{OH})_2} = -15,260 - 151,800 - 68,370 = -235,430 \text{ cal.}$$

It should be noted that the symbols (c) and (l) refer to the substance in the macrocrystalline and liquid state, respectively.

4. The Effect of Temperature on the Heat of Reaction.—Having obtained values for heats of formation at 18 or 25°C ., we can compute the change of ΔH with temperature at constant pressure by means of Eq. (2.25) and, hence, obtain the heat of reaction at any desired temperature, provided that the appropriate heat-capacity data are available. Since the heat capacities of most solids, liquids, and gases are quite adequately expressed as functions of the absolute temperature by means of equations of the form,

$$C_p = a + bT + cT^2 \quad (4.4)$$

or

$$C_p = a + bT - cT^{-2}, \quad (4.5)$$

it follows that the equation

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad (4.6)$$

can be integrated into two useful equations, depending on the form of the heat-capacity function employed. The integrands of Eq. (4.6) corresponding to Eqs. (4.4) and (4.5) are, respectively,

$$\Delta H = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3 \quad (4.7)$$

and

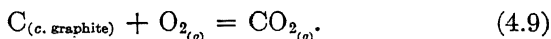
$$\Delta H = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} T^2 + \Delta cT^{-1}. \quad (4.8)$$

In Eqs. (4.7) and (4.8), the Δa 's, Δb 's, and Δc 's represent the individual sums of the a , b , and c terms in the heat-capacity equations for the products, minus the corresponding sums for the reactants. ΔH_0 is the constant of integration and represents the fictitious heat of the reaction in the chosen standard states at the absolute zero, if Eqs. (4.4) and (4.5) were valid down to zero. Equation (4.8) emphasizes one decided advantage to expressing heat capacities in the form of Eq. (4.5), since the somewhat cumbersome T^3 term is thereby eliminated.

5. The ΔH of Formation of CO_2 as a Function of Temperature.

Illustration 2.—The heat of formation of CO_2 is an important constant in the evaluation of heats of formation of organic compounds from their measured heats of combustion. On the basis of the following fundamental thermal data, derive an expression for the heat of formation of CO_2 as a function of temperature and compute ΔH for 18°C .

As a result of the measurements of the heat of combustion of graphite by Dewey and Harper⁵ and by Jessup,⁴ Rossini and Jessup⁶ have selected $\Delta H_{298.1} = -94,030$ cal. as the best value for the reaction



Kelley⁷ gives the following equations for the heat capacities of the substances involved in Eq. (4.9) for temperatures above 0°C .:

$$\text{Graphite: } C_p = 2.673 + 2.617 \times 10^{-3}T - 1.169 \times 10^5 T^{-2}. \quad (4.10)$$

$$\text{O}_2: C_p = 8.27 + 0.258 \times 10^{-3}T - 1.877 \times 10^5 T^{-2}. \quad (4.11)$$

$$\text{CO}_2: C_p = 10.34 + 2.74 \times 10^{-3}T - 1.955 \times 10^5 T^{-2}. \quad (4.12)$$

Solution.—From the form of the heat-capacity equations, Eq. (4.8) should be used. Summing the constant terms in Eqs. (4.10)–(4.12) leads to the following values for the constants in Eq. (4.8):

$$\Delta a = -0.603 \quad \Delta b = -0.135 \times 10^{-3} \quad \Delta c = -1.091 \times 10^5.$$

Consequently,

$$\Delta H = \Delta H_0 - 0.603T - 0.675 \times 10^{-4}T^2 - 1.091 \times 10^5T^{-1}. \quad (4.13)$$

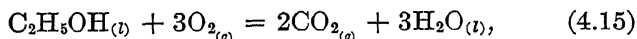
Substituting $\Delta H = -94,030$ and $T = 298.1^\circ\text{K.}$ in Eq. (4.13), yields $\Delta H_0 = -93,480$; consequently the required equation for calculations above 0°C. is

$$\Delta H = -93,480 - 0.603T - 0.675 \times 10^{-4}T^2 - 1.091 \times 10^5T^{-1}. \quad (4.14)$$

At 18°C. , the heat of formation of CO_2 is

$$\begin{aligned} \Delta H_{291} &= -93,480 - 0.603(291.1) - 0.675 \times 10^{-4}(291.1)^2 \\ &\quad - 1.091 \times 10^5(291.1)^{-1} = -94,036 \text{ cal.} \end{aligned}$$

6. Evaluation of Heats of Formation from Heats of Combustion.—If the results of measurements of the heat of combustion of an organic compound containing no other elements but carbon, hydrogen, and oxygen have been properly computed, the value of Q_c represents the heat evolved at room temperature under a constant pressure of 1 atm. when the substance in the form stable at room temperature is burned in O_2 to form gaseous CO_2 and liquid water. For example, the heat of combustion of ethyl alcohol, Q_c , represents the $-\Delta H$ of the process expressed by the equation



for which $\Delta H_{298} = -326,660$ cal./mole of alcohol.⁸ In this particular instance, Rossini⁹ determined the heat of combustion by burning alcohol vapor in air at a constant pressure of 1 atm. and measuring the heat energy by the method of substitution described above. In order to eliminate errors due to possible traces of water in the highly purified alcohol, the mass of alcohol burned in producing the observed heat effect was determined by weighing the CO_2 produced. Hence, one-half the mass of the

CO₂ produced divided by the molecular weight of the CO₂ gives the moles of alcohol equivalent to the observed heat evolution. In 1932, when these results were first reported, the atomic weight of carbon was taken as 12.000; in 1934, the value was recomputed,⁸ with 12.007 for the atomic weight or a molecular weight of 44.007 for CO₂. Thus the heat evolution observed by Rossini corresponded to the burning of a smaller number of moles of alcohol than was recognized at that time; consequently, on the basis of 44.007 for the molecular weight of CO₂, the original Q_c required adjustment by multiplying by the factor 88.014/88.00 in order to obtain the value 326,660 cal./mole previously given.

However, since 1934, the atomic weight of carbon has been changed to 12.01; consequently this value requires further adjustment by the factor 88.020/88.014, which gives 326,680 cal. for the heat of combustion of 1 mole of ethyl alcohol at 25°C. and 1 atm. pressure. Since these experiments were performed, the atomic weight of hydrogen has been changed from 1.0078 to 1.0080; but owing to the analytical procedure employed in Rossini's original experiments, the value of this constant does not affect the value of the molar heat of combustion. The above discussion is intended to emphasize the necessity for a clear understanding of the experimental basis on which heats of combustion are based before even minor adjustments in their values are made.

After the best available value for the heat of combustion has been obtained, the ΔH of formation may readily be computed from the known heats of formation of the products of combustion. Thus, in the case of C₂H₅OH, the ΔH of formation at 25°C. may be computed from the relation indicated by Eq. (4.15),

$$\begin{aligned}\Delta H = -Q_c &= 3\Delta H_{\text{H}_2\text{O}} + 2\Delta H_{\text{CO}_2} - \Delta H_{\text{C}_2\text{H}_5\text{OH}} \\ &= -326,680. \quad (4.16)\end{aligned}$$

Substitution of $\Delta H_{\text{H}_2\text{O}} = -68,315$ and $\Delta H_{\text{CO}_2} = -94,030$ in this equation gives $-66,325$ cal. for the heat of formation of 1 mole of liquid C₂H₅OH at 25°C. The above value of $\Delta H_{\text{H}_2\text{O}}$ represents Rossini's¹⁰ value of $-68,313$ for liquid water, corrected by the ratio 18.0160/18.0156 to allow for the new atomic weight of hydrogen, 1.0080 instead of 1.0078.

Rossini⁸ gives the heat of formation of $C_2H_5OH_{(l)}$ at $25^\circ C.$ from so-called β graphite as $-66,750$ cal./mole. In arriving at the value $-66,325$ cal., it should be noted that the equation used was

$$\Delta H' = Q_c \left(\frac{88.020}{88.014} \right) + 3\Delta H_{H_2O} \left(\frac{18.0160}{18.0156} \right) + 2\Delta H'_{CO_2}, \quad (4.17)$$

whereas Rossini used the equation

$$\Delta H = Q_c + 3\Delta H_{H_2O} + 2\Delta H_{CO_2}. \quad (4.18)$$

In these equations the primes indicate the new values for the heats of formation of C_2H_5OH and CO_2 . Thus, it can be seen that there is no simple factor that can be used to correct the earlier heat of formation of alcohol in order to obtain the new value.

7. Correcting Heats of Formation from Diamond to Graphite.

Illustration 3.—The accuracy of some of the older heats of combustion data used to compute heats of formation of the simpler organic compounds recorded in Bichowsky and Rossini is of such degree, that the effect of small changes in the atomic weight of carbon on computed heats of formation may be neglected. Furthermore, since the acceptance of graphite⁶ as the standard state for carbon, the tabulated values of Bichowsky and Rossini based on diamond as the standard state will eventually be supplanted by values based on the new heat of combustion of graphite. Show, by actually recalculating the values for the heats of formation of $HCOOH_{(l)}$ and $HCOOCH_3_{(g)}$ given in Bichowsky and Rossini with reference to graphite as the standard state of carbon, that the corrected heats of formation ($\Delta H'$) are given by the following expression:

$$\Delta H'_{291} = \Delta H_{B-R} - N(\Delta H_D - \Delta H_{Gr})_{CO_2}, \quad (4.19)$$

where ΔH_{B-R} = the heat of formation ($-Q_f$) of the substance at $18^\circ C.$, as recorded in Bichowsky and Rossini.

ΔH_D = the heat of formation of CO_2 from diamond ($-94,450$ cal.).

ΔH_{Gr} = the heat of formation of CO_2 from graphite at $18^\circ C.$ ($-94,036$ cal.).

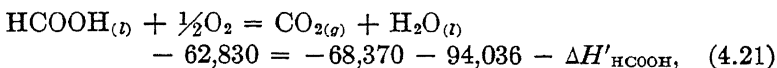
and N = number of carbon atoms in the molecule.

Solution.—Substitution of the appropriate values in Eq. (4.19) gives the following equation for computing the approximate correction to heats of formation based on diamond, but neglecting changes in atomic weights:

$$\Delta H'_{291} = \Delta H_{B-R} + 414N. \quad (4.20)$$

a. $\text{HCOOH}_{(l)}$

Three independent experimental determinations of the heat of combustion of liquid formic acid are listed (B-R, p. 236): 63,000, 62,500, and 63,000 cal./mole. The average value 62,830 equals $-\Delta H_{291}$ for the reaction

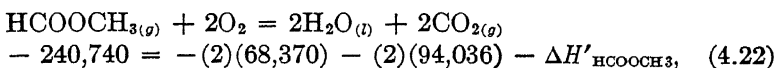


from which $\Delta H' = -99,576$ cal./mole $= -Q_f$. The value recorded in B-R is $-100,000$ cal. From Eq. (4.20) the corrected value is

$$\Delta H' = -100,000 + 414 = -99,586 \text{ cal.}$$

b. $\text{HCOOCH}_{3(g)}$

Bichowsky and Rossini selected 240,740 cal. as the average of the three measured heats of combustion: 241,000, 240,900, 240,200 cal./mole, corresponding to the reaction



from which $\Delta H' = -84,072$ cal./mole $= -Q_f$. The value recorded in B-R is $-84,900$ cal. From Eq. (4.20) the corrected value is

$$\Delta H' = -84,900 + 2(414) = -84,072.$$

Although Eq. (4.19) for converting from heats of formation based on diamond to heats of formation based on graphite is not precise, it is probably within the precision of the data obtained by the earlier investigators. The results of modern investigators in this field should also be corrected systematically for changes in atomic weights when required, after reviewing the bases for the reported results.

The evaluation of heats of combustion of organic compounds containing elements in addition to carbon, hydrogen, and oxygen

is complicated by the necessity for determining the final physical and chemical state of these other elements. For example, in most cases the observed heats of combustion of organic compounds containing chlorine refer to the formation of dilute aqueous hydrochloric acid, but in some cases the formation of HCl gas has been reported. Furthermore, unless the quantity of H₂O originally introduced into the bomb is recorded, it is impossible to calculate the final concentration of the HCl, and hence to allow for any thermal effect due to heat of dilution. The combustion of organic compounds of sulphur usually results in the formation of a dilute solution of sulphuric acid, but in some cases the formation of gaseous SO₂ has been reported. Heats of combustion of nitrogen containing compounds are employed on the basis that only elementary nitrogen is produced, although in some cases slight amounts of nitric acid are formed from nitrogen oxides and water. In general, heats of formation computed from heats of combustion of the more complex organic compounds are not very precise at present.

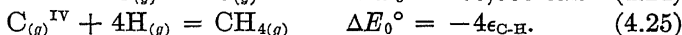
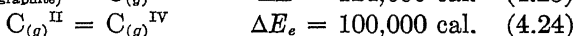
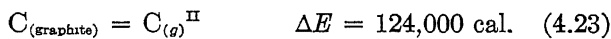
8. Direct Measurements of Heats of Reaction.—In view of the uncertainties introduced into the calculation of heats of formation from heats of combustion of all but the simplest organic molecules, it has been found simpler and more reliable to measure directly the heats of certain types of reactions of theoretical interest, instead of the heats of formation of the individual substances involved. These investigations have been carried out by Kistiakowsky and coworkers,¹¹⁻¹⁸ and have thus far been chiefly confined to measuring the heat evolved when a variety of unsaturated aliphatic and aromatic compounds add from one to four molecules of H₂ per molecule of compound, in the presence of a suitable catalyst at 82°C. In the same manner, Conn, Kistiakowsky, and Smith¹⁹ have measured the heat evolution accompanying the addition of Br₂ to a number of olefinic compounds and the heat of addition of Cl₂ to ethylene. Since the accuracy with which the heats of formation of either the initial or final compounds are known is good and improved values are steadily being obtained, the accuracy of the heats of formation of the unknown compounds should be quite satisfactory. Obviously, the field of application of this method of direct measurement is restricted to types of reactions which can be made to take place at a rate convenient for calorimetric study

and which are not complicated by the occurrence of undesirable side reactions.

9. Indirect Measurements of Heats of Reaction.—Accurate values for enthalpy changes accompanying physical or chemical changes of state may also be derived from the temperature coefficient of the standard free-energy change corresponding to the reaction involved. In the case of chemical reactions the procedure is to express the free-energy change either in terms of the observed equilibrium constant of the reaction or the observed electromotive force corresponding to the reaction. The observed change of K or E with the absolute temperature is then treated by the methods described in Chap. VI in order to evaluate the desired heat of reaction or heat of formation.

10. Evaluation of Heats of Formation from Bond Energies.—In view of the widely conflicting values of so-called "bond energies," deduced from thermochemical data and from kinetic studies on thermal and photochemical reactions, it would seem that values of heats of formation computed from bond energies have little physical significance. However, in certain cases, particularly in considerations pertaining to members of homologous series, the concept of bond energies may be of some assistance in estimating heats of formation of undetermined members of the series. The basis for most compilations of bond energies involving carbon is the equivalence of the four CH bonds in methane. With this assumption and a definite choice of value for the energy of sublimation of graphite and the energy of excitation necessary to raise divalent carbon to the quadrivalent state, it is possible to proceed from compound to compound involving only one additional new bond at a time, and to obtain a set of bond energies of good internal consistency but questionable physical significance.

For example, the value for the C-H linkage may be derived from a consideration of the following thermochemical equations:



Equation (4.25) defines the energy of the C-H bond. It is one-fourth the energy required to decompose gaseous methane into normal gaseous atoms of hydrogen and carbon at the

absolute zero. In view of the unsoundness of the assumption of the equivalence of the four C-H bonds in methane and the uncertainties in the heat of sublimation of graphite, corrections of ordinary heats of formation at room temperature down to 0°K. are unwarranted. Using the B-R value for the heat of dissociation of H₂ and -17,807 for the ΔH of formation of CH₄ at 18°C. gives

$$\Delta E_0^\circ = -4\epsilon_{\text{C-H}} = -17,807 - 4(51,900) - 224,000,$$

from which

$$\epsilon_{\text{C-H}} = 112,350 \text{ cal. as the energy of the C-H linkage.}$$

In a similar manner, the energy of the C-C linkage may be computed from the heat of formation of ethane (-20,195 cal.) and the equation

$$\begin{aligned} 2\text{C}_{(g)}^{\text{IV}} + 6\text{H}_{(g)} &= \text{C}_2\text{H}_{6(g)} & \Delta E_0^\circ &= -(6\epsilon_{\text{C-H}} + \epsilon_{\text{C-C}}), \quad (4.26) \\ -6\epsilon_{\text{C-H}} - \epsilon_{\text{C-C}} &= -20,195 - 6(51,900) - 2(224,000), \\ \epsilon_{\text{C-C}} &= 105,500 \text{ cal.} \end{aligned}$$

In this manner, a table of bond energy values may be built up, which can in some cases be used to estimate heats of formation from the relation

$$\Delta H_f = -\sum \nu_i \epsilon_i + \sum \Delta H_A, \quad (4.27)$$

where ΔH_f = standard heat of formation of compound in gaseous state based on the assumption of bond additivity.

$\sum \Delta H_A$ = sum of heats of formation of gaseous atoms produced by complete decomposition of compound.

ν_i = number of bonds of the i th type.

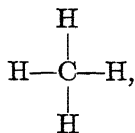
ϵ_i = energy of i th type of linkage.

For example, the heat of formation of gaseous propane may be estimated from the unsound assumption that all eight C-H bonds are equivalent: therefore,

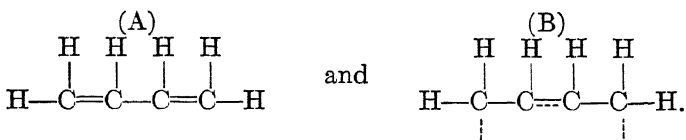
$$\begin{aligned} \Delta H_f &= -(8)(112,350) - 2(105,500) + 8(51,900) + 3(224,000), \\ \Delta H_f &= -22,600 \text{ cal./mole as compared with the experimental} \\ &\hspace{15em} \text{value of } -24,750 \text{ cal.} \end{aligned}$$

The extension of this method of estimating heats of formation to such compounds as butadiene and benzene is complicated by the phenomenon of resonance. This complication arises because,

unlike methane, the structure of which can be represented by the single valence bond structure



where each bonding sign represents the bonding pair of electrons shared between the carbon atom and a hydrogen atom, the electronic structure of butadiene is something in between the structures



There are many cases of this kind in organic as well as inorganic chemistry, where no unique scheme of electron pairing is possible and the molecule is said to resonate between each of the various possible structures. This does not necessarily mean that the molecule is fluctuating from one structure to another at a very high frequency, but rather that the real state of the molecule is a combination of the various possible structures. This "combination state" has a lower potential energy than either of the individual states and is therefore more stable than the individual states. Hence the phenomenon of resonance is important from the thermochemical as well as the chemical standpoint, since heats of formation of "resonating" compounds are higher than the equivalent nonresonating compounds.

It is obvious, therefore, that the possibility of resonance introduces a further uncertainty into the estimation of heats of formation from bond energies, in addition to the general unsoundness of the assumption of simple bond additivity. The condition for the existence of resonance is that the electronic structure of a molecule can be depicted in two or more ways in which the positions of the atoms remain unchanged and the energies of the various states do not differ greatly from one another. Since one of the principal methods for detecting the existence of resonance is based on observed heats of formation, it is apparent that reversal of the process to estimate the heat of formation of a

compound, which may or may not resonate, is impossible. For example, Pauling and coworkers²⁰⁻²² have estimated resonance energies by taking the difference between the energy of the molecule computed from observed heats of formation and the energy computed from additivity of bond energies. Such figures, however, are believed to be of more qualitative than quantitative significance.²³

A more reliable method for detecting the existence of resonance is based on the measurements of internuclear distances by means of electron diffraction experiments. The essence of this method is the observation that internuclear distances between any pair of atoms decrease with the number of pairs of electrons holding the atoms together. Thus, the distance between two atoms held together by a triple bond is smaller than that for a double bond, which in turn is smaller than that for a single-bond distance. In some cases, results of dipole moment measurements on gaseous molecules and band spectrum studies afford evidence of the existence or nonexistence of the phenomenon of resonance. The following data, taken from the paper by Pauling and Brockway,²⁴ illustrate the dependence of internuclear distance on bond type for ordinary covalent linkages:

COVALENT RADII
(cm. $\cdot 10^{-8}$)

| Bond | C | N | O | F | Si | P | S | Cl |
|-------------|------|------|------|------|------|------|------|------|
| Single..... | 0.77 | 0.70 | 0.66 | 0.64 | 1.17 | 1.10 | 1.04 | 0.99 |
| Double..... | 0.67 | 0.61 | 0.57 | 0.55 | 1.06 | 1.00 | 0.95 | 0.90 |
| Triple..... | 0.60 | 0.55 | 0.51 | | 0.99 | 0.93 | 0.88 | |

When the absence of resonance in the molecule under consideration has been definitely established by any of the above methods, a rough estimate of the heat of formation of the compound may be made from bond energies deduced from heats of formation of compounds containing similar linkages.

11. Estimation of the ΔH of Formation of Sulphur Dichloride.

Illustration 4.—A direct calorimetric determination of the heat of formation of gaseous sulphur dichloride (SCl_2) is not available, but Bichowsky and Rossini give the following pertinent heats of formation:

| Compound | ΔH_{291} |
|------------|------------------|
| S_2Cl_2 | -5,650 calories |
| $S_{(g)}$ | +66,300 calories |
| $S_{8(g)}$ | +20,000 calories |

Estimate a value for the heat of formation of SCl_2 .

Solution.—The electron diffraction patterns of gaseous S_2Cl_2 and SCl_2 give²⁵ $1.99 \cdot 10^{-8}$ and $2.00 \cdot 10^{-8}$ cm. for the S-Cl distance²⁶ in these compounds and 2.05\AA for the S-S distance in S_2Cl_2 . Since the observed values are quite close to the so-called "standard" values, it would appear that both these compounds possess ordinary single-bonded S-Cl and S-S linkages and very little, if any, double-bonded resonance states. Accordingly, the heats of formation of S_2Cl_2 and $S_{8(g)}$ may be used to estimate the energies of the S-S and S-Cl bonds.

In accordance with the foregoing data on heats of formation, the following thermochemical equations may be set up:

$$S_{Rh} = S_{(g)} \quad \Delta H = 66,300. \quad (4.28)$$

$$8S_{Rh} = S_{8(g)} \quad \Delta H = 20,000. \quad (4.29)$$

$$2S_{Rh} + Cl_{2(g)} = S_2Cl_{2(g)} \quad \Delta H = -5,650. \quad (4.30)$$

$$\frac{1}{2}Cl_{2(g)} = Cl_{(g)} \quad \Delta H = 28,900. \quad (4.31)$$

The energy of the S-S linkage may, therefore, be estimated by substituting the appropriate values from Eqs. (4.28) and (4.29) in Eq. (4.27). Consequently,

$$20,000 = -8\epsilon_{S-S} + 8(66,300),$$

$$\epsilon_{S-S} = 66,300 - \frac{20,000}{8} = 63,800 \text{ cal.}$$

The energy of the S-Cl linkage may then be estimated from this value and Eqs. (4.30) and (4.31) in the same manner,

$$-5,650 = -(2\epsilon_{S-Cl} + 63,800) + 2(66,300) + 2(28,900),$$

$$\epsilon_{S-Cl} = 66,125 \text{ cal.}$$

The ΔH corresponding to the desired reaction is, therefore,

$$\Delta H_f = -2(66,125) + 2(28,900) + 66,300 = -8,150 \text{ cal.}$$

This value for the heat of formation of SCl_2 is based on the assumptions that the two S-Cl linkages are identical in this compound and are identical with these linkages in S_2Cl_2 . Since such assumptions are only partially true, it is difficult to estimate the

accuracy of such a calculation. In some cases, values estimated by this type of procedure are quite good and at other times, worthless. Very little additional certainty would be gained by correcting all values to the absolute zero and using bond energies in their defined sense; hence calculations of this sort might just as well be reduced to the minimum amount of labor.

12. Stability of Hydrocarbon Molecules.—On the basis of his determination of the heats of combustion of the five isomeric hexanes²⁷ and a review of existing data on other hydrocarbons, Rossini²⁸ has suggested that the following factors operate to impart greater stability to hydrocarbon molecules:

- a. Resonance.
- b. Minimum departure of the bond angles from the tetrahedral value ($109^{\circ}28'$).
- c. Maximum compactness of the carbon skeleton.
- d. Minimum of repulsion between nonbonded atoms.

In a rough qualitative way, these statements imply that, for any given pair of isomers, the isomer conforming more fully to these conditions will have the larger heat of formation, *i.e.*, greater heat evolution accompanying the formation from the elements in their standard states. It should be noted, however, that comparisons of stability based on energies or heats of formation are reliable only when performed at the absolute zero; otherwise, free-energy data should be employed.

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CHAPTER V

EQUILIBRIUMS IN PHYSICAL PROCESSES AND THE FREE-ENERGY CHANGE

1. Conditions for Equilibrium.—Treatises dealing with the subject of thermodynamics in its broader, more theoretical aspects usually state, as the necessary and sufficient conditions for equilibrium, that the internal energy of the system must be a minimum and the entropy a maximum. Accordingly, systems not already in equilibrium will tend to move in a direction that will fulfill these two requirements. Since chemists are usually interested in processes occurring at constant pressure and temperature, it follows from the definition of the free-energy function,

$$F = H - TS = E - TS + PV, \quad (5.1)$$

and these two conditions, that F must also decrease in moving toward equilibrium. Therefore, in order that a process may occur under these conditions, it is necessary for the free energy of the final state, F_2 , to be less than the free energy of the initial state, F_1 , or

$$F_2 < F_1 \quad \text{and} \quad F_2 - F_1 < 0. \quad (5.2)$$

That is, ΔF must be negative for a process to be spontaneous. When the free energy of the final state equals the free energy of the initial state, the system is in a state of equilibrium with respect to transformations between these two states; since by this criterion a spontaneous change is impossible, the condition for equilibrium at constant pressure and temperature is

$$\Delta F = 0. \quad (5.3)$$

Furthermore, if the thermodynamic system under consideration consists of several phases, the molar free energies (or partial molar free energies in solutions) of its individual components will be equal throughout the system, regardless of the physical state, when the system is at equilibrium.

Since the free-energy function will be used to predict the equilibrium of physical and chemical processes occurring under constant temperature and pressure, it will be necessary to provide the tools required for predicting the changes in equilibrium when the given processes are subjected to different conditions of temperature and pressure. Differentiation of Eq. (5.1) with respect to pressure at constant temperature yields

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T - T \left(\frac{\partial S}{\partial P}\right)_T + P \left(\frac{\partial V}{\partial P}\right)_T + V, \quad (5.4)$$

and differentiation of Eq. (1.8) with respect to pressure gives

$$\left(\frac{\partial E}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T. \quad (5.5)$$

Adding Eqs. (5.4) and (5.5) gives the desired relation

$$\left(\frac{\partial F}{\partial P}\right)_T = V. \quad (5.6)$$

In a similar manner,

$$\left(\frac{\partial F}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P - T \left(\frac{\partial S}{\partial T}\right)_P - S. \quad (5.7)$$

But for a reversible process at constant pressure,

$$dS = \frac{dQ}{T} = C_p \frac{dT}{T} = \left(\frac{\partial H}{\partial T}\right)_P \frac{dT}{T}. \quad (5.8)$$

Hence

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P. \quad (5.9)$$

Subtracting Eq. (5.9) from (5.7) yields

$$\left(\frac{\partial F}{\partial T}\right)_P = -S. \quad (5.10)$$

Eqs. (5.6) and (5.10) will be found to be the two most useful equations in thermodynamics. Substituting for S its value from Eq. (5.1) yields the equation

$$\left(\frac{\partial F}{\partial T}\right)_P = \frac{F - H}{T}. \quad (5.11)$$

The form in which Eq. (5.11) is commonly employed is

$$\frac{d(\Delta F/T)}{dT} = \frac{-\Delta H}{T^2}. \quad (5.12)$$

2. The Fugacity.—As pointed out in Sec. 1, if the molar free energy in state (2) of a system is less than the molar free energy of the system in the initial state (1), the system must eventually pass from (1) to (2); thus the molar free energies serve as a quantitative measure of the tendency of the system to pass from one state to another. This tendency is termed the “escaping tendency.” Furthermore, since the molar free energies of the individual components of a system composed of more than one phase must be equal throughout the system when equilibrium is attained, it can be said that the escaping tendency of each component is the same throughout the system. When liquid or solid solution phases are included within the system, it is necessary to use the partial molar free energies of the components as a measure of the escaping tendency.

Now it turns out, as a matter of practical experience, that the numerical application of free energies to physical and chemical problems is considerably facilitated if another quantity, bearing the following algebraic relation to the molar free energy, is employed in its place as a measure of the escaping tendency:

$$RT \ln f = F - B, \quad (5.13)$$

in which the defined quantity f , commonly employed as a measure of the escaping tendency in numerical calculations, is called the “fugacity.” F is the molar free energy or partial molar free energy of the substance. B is a constant at any temperature and need not be considered further, since it drops out when the difference in molar free energies between two states at the same temperature is evaluated, as shown by the equation

$$\Delta F = F_2 - F_1 = RT \ln \frac{f_2}{f_1}. \quad (5.14)$$

A physical basis for the form of Eq. (5.13), defining the fugacity, may be found as follows:

From Eq. (5.6) it can be seen that, when 1 mole of a perfect gas is expanded from a pressure P_1 to P_2 under isothermal conditions, the free-energy change is given by the equation

$$\Delta F = F_2 - F_1 = \int V dP = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} \quad (5.15)$$

A comparison of Eq. (5.14) with (5.15) shows that the pressure of a perfect gas is identical with the true escaping tendency or fugacity, whereas for real gases the pressure measures the escaping tendency only in the limit at zero pressure, when all gases approach perfect behavior. This may readily be shown by the fact that substitution of any equation of state for actual gases in the equation

$$\left(\frac{\partial F}{\partial P}\right)_T = V$$

does not yield Eq. (5.15). Thus, since the idea of a mechanical pressure as a measure of an escaping tendency is easy to grasp, the equivalence between pressures and fugacities in the limit increases the physical reality of what might otherwise appear to be an unnecessarily complicated way of defining fugacities [Eq. (5.13)].

For accurate work with real gases under finite pressures it is necessary to employ the equation

$$RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} V dP \quad (5.16)$$

in conjunction with an appropriate equation of state or actual PVT data in order to evaluate fugacities (see L-R, Chap. XVII). For most purposes it is permissible to substitute pressures for fugacities when dealing with systems at moderate pressures of, say, less than 3 or 4 atm.; but, in general, Eq. (5.16) must be employed.

Two convenient and reasonably accurate equations of state for the computation of fugacities are

$$PV = NRT - N\alpha P \quad (5.17)$$

$$PV = CNRT, \quad (5.18)$$

where N represents the total number of moles in the volume V at the pressure P , and α is a coefficient measuring the deviation of the gas from ideality and is a function of T and P . In Eq. (5.18) the constant C is called the "coefficient of compressibility" and is also a function of T and P . As the pressure is reduced to

zero, the coefficient of compressibility approaches unity, and α approaches zero. The two coefficients are connected by the relation

$$\alpha = \frac{RT}{P} (1 - C). \quad (5.19)$$

Although Eqs. (5.17) and (5.18) are among the simplest equations of state for real gases, substitution in Eq. (5.16) produces an integral, which cannot be integrated analytically but must be evaluated by graphical integration. Fortunately, for moderately high pressures the Berthelot equation of state may be employed in order to obtain the integrand of Eq. (5.16), as shown in the illustrative problem that follows.

3. Calculation of the Fugacity of a Berthelot Gas. *Illustration 1.*—Compute the fugacity of CO_2 at 100°C . and 200 atm. pressure, on the assumption that the gas conforms to the Berthelot equation of state.

Solution.—Substituting Eq. (2.19) in (5.16) gives

$$RT \ln \frac{f_2}{f_1} = RT \int_{P_1}^{P_2} \left[1 + \frac{9}{128} \frac{PT_c}{P_c T} \left(1 - \frac{6T_c^2}{T^2} \right) \right] \frac{dP}{P}. \quad (5.20)$$

Substituting the pressure P , at which the fugacity f is required, and the low pressure P° , such that $f_1 = P^\circ$ as P° approaches zero, for the limits of integration gives

$$\ln \frac{f}{P^\circ} = \ln \frac{P}{P^\circ} + \frac{9}{128} \frac{T_c}{P_c T} \left(1 - \frac{6T_c^2}{T^2} \right) (P - P^\circ), \quad (5.21)$$

and consequently

$$\ln \frac{f}{P} = \frac{9}{128} \frac{T_c}{P_c T} \left(1 - \frac{6T_c^2}{T^2} \right) P. \quad (5.22)$$

Substituting

$$\begin{aligned} T &= 373^\circ\text{K}. & P_c &= 73 \text{ atm.} \\ T_c &= 304.2^\circ & P &= 200 \text{ atm.} \end{aligned}$$

in Eq. (5.21) gives

$$\frac{f}{P} = 0.624 \quad \text{or} \quad f = 125 \text{ atm.}$$

At 100°C . and 200 atm. the fugacity of CO_2 computed from Berthelot's equation is 125 atm. or, as it is sometimes said,

CO₂ has an activity coefficient of 62.4 per cent under these conditions.

4. Activity Coefficient and Compressibility Charts.—By introducing the reduced temperature, T/T_c , and the reduced pressure, P/P_c , into Eq. (5.22), the following equation is obtained for computing the so-called activity coefficient of gases:

$$\ln \gamma = \ln \frac{f}{P} = \frac{9}{128} \frac{P_r}{T_r} \left(1 - \frac{6}{T_r^2} \right). \quad (5.23)$$

According to this equation, the activity coefficients of gases should be a universal function of the reduced temperature and reduced pressure, and independent of the nature of the particular gas to the extent that all gases obey the same equation of state. On this basis, charts of the ratio f/P vs. the reduced pressure for various values of the reduced temperature have been prepared,¹ which permit rapid estimations of the fugacities of pure gases over a wide range of pressures and temperatures (Fig. 3). Data used to plot the chart have been based on experimental PVT data, reported in the literature for a number of widely different types of gases. Although such charts are not too accurate for all gases under all conditions, estimated values are good enough for most purposes. This same method of correlation has been employed by several investigators² for the presentation of data on compressibilities, defined by the equation of state

$$PV = CNRT.$$

Values of compressibilities obtained from such charts² (Figs. 4 and 5) are of considerable value in estimating actual gas volumes at a given pressure and temperature, when only the critical constants of the gas are known.

In the case of mixtures of gases it is customary to assume, as a matter of practical expediency, that (1) the fugacity of any component of the mixture at a total pressure P is equal to $f_i^\circ N_i$, where f_i° is the fugacity of the pure i th component at the pressure P , and N_i is its mole fraction, and that (2) the activity coefficient (f_i/P_i) of the i th component of the mixture at the total pressure P is equal to the activity coefficient of the pure component at the pressure P . These assumptions are only partially true, but they are almost unavoidable in view of the present state of development of the subject.

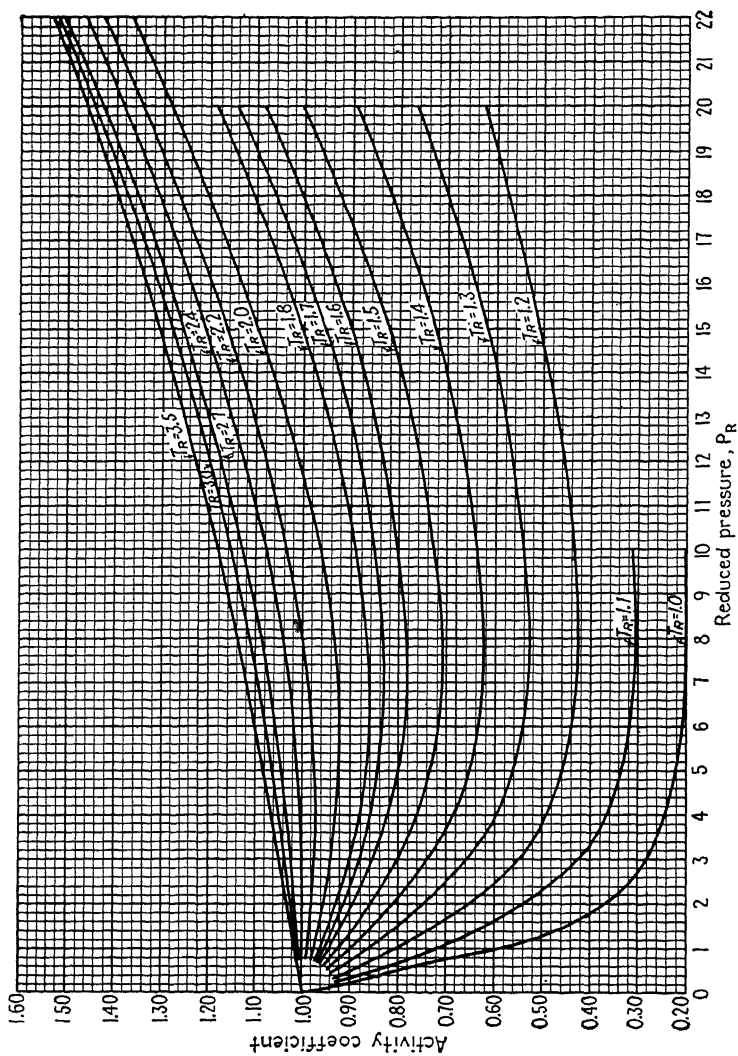


Fig. 3.—Activity coefficients of gases at elevated pressures.

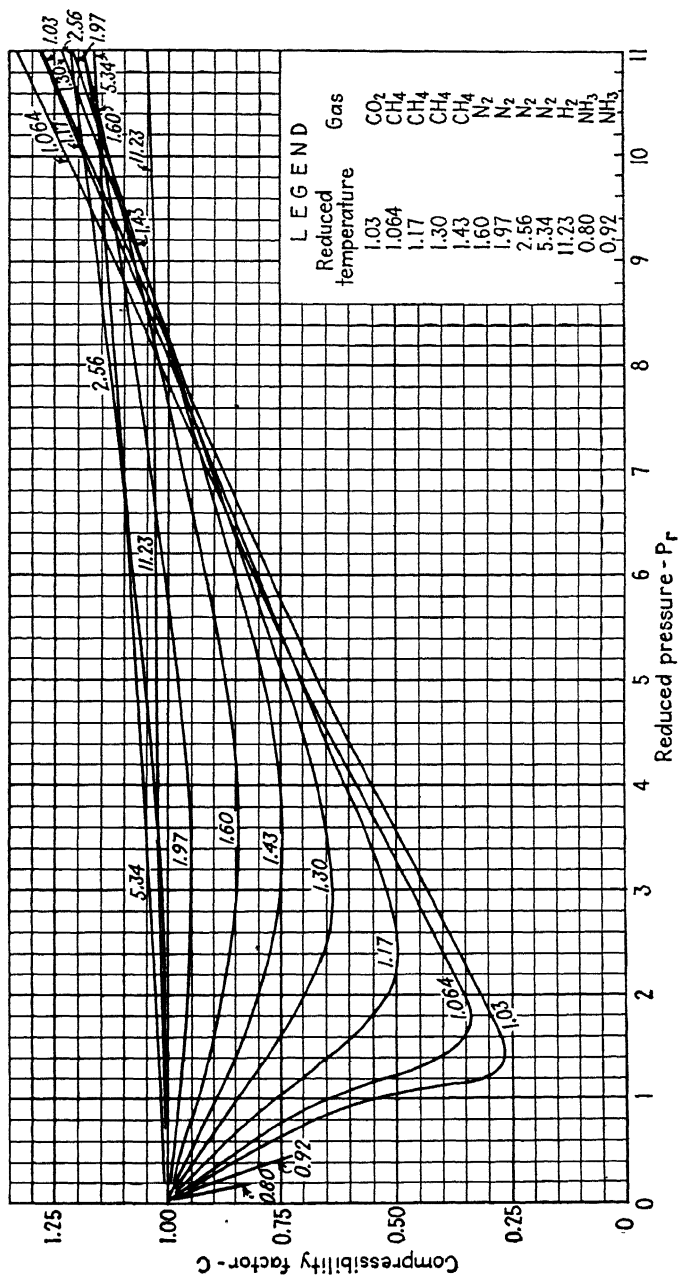


Fig. 4.—Compressibility factors at intermediate pressures.

A number of relations have been proposed for estimating the compressibilities of mixtures of gases. When the critical constants of the individual components of the mixture are known, the following relation, proposed by Kay³ for estimating the critical constants of the mixture, is probably as good as any other method:

$$(T_c)_{\text{mix}} = (T_c)_1 N_1 + (T_c)_2 N_2 + \dots \quad (5.24)$$

$$(P_c)_{\text{mix}} = (P_c)_1 N_1 + (P_c)_2 N_2 + \dots \quad (5.25)$$

where $T_c \dots$, $P_c \dots$ are the critical constants of the pure components and the N 's are the respective mole fractions. The

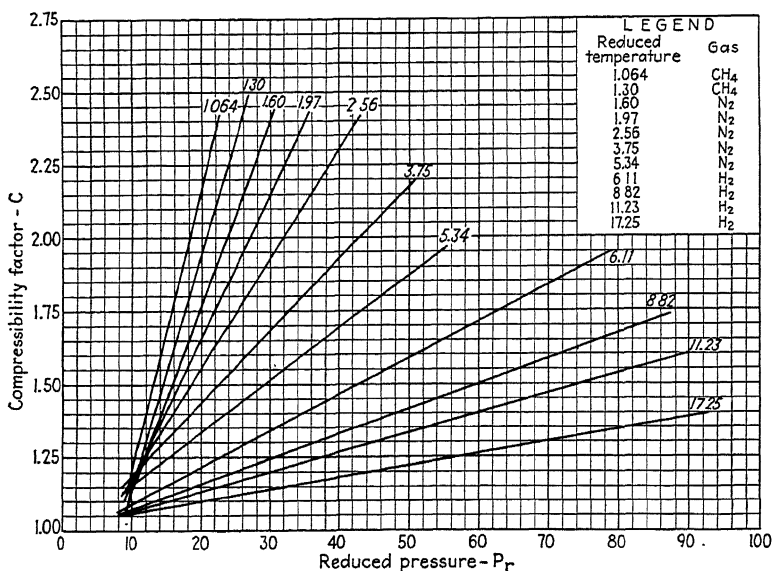


FIG. 5.—Compressibility factors at high pressures.

reduced temperature and pressure of the mixture is then computed from these pseudocritical constants and the corresponding values of compressibilities read from Fig. 4. Beattie⁴ has proposed a much more elaborate and accurate procedure for estimating *PVT* data for mixtures of gases, based on the use of weighted constants of the Beattie-Bridgman equation of state. Since the method requires a knowledge of all five constants for each component, the application is restricted to gases for which these constants are known.

5. Equilibriums between Two Phases of a Pure Substance.—

From the condition that the molar free energies of the components of a system must be equal throughout the system at equilibrium, and that any changes in P and T must produce corresponding changes in the free energies of the substance in all phases in order to preserve the equilibrium, it follows that

$$dF_1 = dF_2. \quad (5.26)$$

By expressing these total differentials in terms of their partial differentials with respect to T and P , substituting the appropriate values for these partials given by Eqs. (5.6) and (5.10), and introducing them into Eq. (5.26) (L-R, p. 180), the following equation is obtained:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}. \quad (5.27)$$

If the system is under its own vapor pressure p , the equation is then written

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}. \quad (5.28)$$

In this equation ΔH represents the enthalpy change accompanying the transfer of 1 mole of the substance from the first to the second of the two phases in equilibrium, at the pressure p , and the temperature T ; ΔV represents the volume of 1 mole of the substance in the second phase, minus the molar volume in the first phase, at the pressure p , and temperature T . When the two phases in equilibrium are liquid and vapor, ΔH is the molar heat of vaporization; when solid and liquid, ΔH is the molar heat of fusion; and for the equilibrium between two modifications of a pure solid, ΔH is the molar heat of transition. It is important to note that Eq. (5.27) applies only to a univariant system, *i.e.*, one in which the pressure is fixed when the temperature is chosen or vice versa. This same equation also applies to the change of eutectic temperature of a binary system with pressure, since at the eutectic point such a system is a univariant system.

Equation (5.28) is frequently employed in problems dealing with liquid-vapor equilibriums, where the vapor is assumed to be a perfect gas at ordinary pressures and the molar volume of the liquid is assumed to be negligible compared to that of the gas; hence

$$\frac{dp}{dT} = \frac{\Delta H}{T \left(\frac{RT}{p} \right)}$$

and

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}. \quad (5.29)$$

In this form Eq. (5.29) applies approximately to the equilibrium between a liquid and its vapor, where both phases are under the vapor pressure of the liquid at the temperature T . In actual practice the liquid phase is usually under a constant pressure P , other than the vapor pressure p . For this case Lewis and Randall (L-R, p. 183) derive the following equation for the equilibrium between the two phases:

$$\left(\frac{\partial p}{\partial T} \right)_P = \frac{\Delta H}{TV_g}. \quad (5.30)$$

Here p represents the vapor pressure, P the constant head on the liquid, V_g the volume of 1 mole of the vapor, and ΔH the enthalpy change accompanying the transfer of 1 mole from the liquid at the pressure P , to the gas phase at the pressure p . Assuming the vapor to be a perfect gas leads to the equation

$$\left(\frac{\partial \ln p}{\partial T} \right)_P = \frac{\Delta H}{RT^2}. \quad (5.31)$$

Equations (5.29) and (5.31) are different, since the differential coefficients are obviously not identical, and the two ΔH 's are different in physical significance, if not numerically.

Another case of interest to the chemist is the two-phase equilibrium of a pure substance, in which the pressures on both phases vary while maintaining the temperature of the system as a whole constant. From the condition that the molar free energies must remain equal in both phases in order to preserve the equilibrium, it follows that

$$\left(\frac{\partial P_1}{\partial P_2} \right)_T = \frac{V_2}{V_1}, \quad (5.32)$$

where the V 's represent the molar volumes of the substance in the two phases. If the vapor in equilibrium with the liquid

phase is at a moderate pressure so that ideal gas behavior may be assumed, Eq. (5.32) becomes

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{V_l}{RT/p},$$

or

$$\left(\frac{\partial \ln p}{\partial P}\right)_T = \frac{V_l}{RT}, \quad (5.33)$$

where V_l is the molar volume of the liquid phase. Thus at room temperature the vapor pressure of water increases at the rate of $(100 \times 18.0)/(82.06 \times 298.1) = 0.0734$ per cent per atmosphere. At higher pressures, the equation

$$PV = CRT$$

may be used to substitute for the gas volume, and the equation

$$V_l = V_0(1 - \beta P), \quad (5.34)$$

for the liquid volume. In this equation β is the isothermal coefficient of compressibility and is defined by the equation

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T. \quad (5.35)$$

Hence Eq. (5.33) becomes

$$\left(\frac{\partial \ln p}{\partial P}\right)_T = \frac{V_0}{RT} \left(\frac{1 - \beta P}{C}\right). \quad (5.36)$$

This equation may be integrated by plotting the function $(1 - \beta P)/C$ against the pressure and multiplying the area under the curve from zero to P by V_0/RT , in order to obtain $\ln p/p_0$. p_0 is the vapor pressure of the pure substance at the temperature T , with zero external pressure on the liquid; p is the vapor pressure at the same temperature, when the liquid phase is under the pressure P .

The value of the vapor pressure, computed by this method, represents the actual mechanical pressure as measured by some suitable gauge, and is not to be confused with the fugacity of the substance, which is equal to the product of the activity coefficient by the vapor pressure. Methods have already been discussed for computing the dependence of vapor pressure on temperature

and pressure, and for computing the dependence of fugacity on pressure [see Eq. (5.22)] and it is, therefore, of interest to investigate the change of fugacity with temperature at constant pressure.

From Eq. (5.14) the difference between the free energy of a substance, at such a low pressure that the fugacity equals the pressure, and the free energy in the state of interest is

$$F' - F = RT \ln \frac{f'}{f}. \quad (5.37)$$

In this equation the primed symbols indicate the low-pressure state. By differentiating this equation with respect to temperature, while maintaining the pressure on each state constant—noting that $\partial \ln f' / \partial T$ at constant pressure does not change because f' equals the pressure—and substituting for $(\partial F / \partial T)_P$ in terms of (5.11), the following equation is obtained

$$\left(\frac{\partial \ln f}{\partial T} \right)_P = \frac{H' - H}{RT^2}, \quad (5.38)$$

where $H' - H$ is the enthalpy change accompanying the vaporization of 1 mole of the substance into a vacuum from the state in question.

6. Calculation of Change of Activity Coefficient with Temperature. *Illustration 2.*—In illustration 1 it was found that the activity coefficient of CO_2 at a pressure of 200 atm. and 100°C . equals 0.624. Using Eq. (5.38), compute the activity coefficient of the CO_2 at 130°C . and 200 atm.

Solution.—Equation (5.38) may readily be applied if a value for the heat of vaporization of CO_2 from 200 atm. down to zero pressure at 100°C . may be obtained. A good approximation to this quantity may be computed from Eq. (2.20), based on the thermodynamic relation expressed by Eq. (2.18) and the Berthelot equation of state. Substituting the proper limits in (2.20) gives

$$H_{200} - H_0 = \frac{9RT_c}{128P_c} \left(1 - \frac{18T_c^2}{T^2} \right) P, \quad (5.39)$$

and substituting

$$\begin{aligned} T &= 373^\circ\text{K}. & P_c &= 73 \text{ atm.} \\ T_c &= 304.2^\circ\text{K}. & P &= 200 \text{ atm.} \end{aligned}$$

in this equation gives $H_{200} - H_0 = -1,282$ cal./mole, or the value of $H' - H$ to be substituted in Eq. (5.38) equals $+1,282$ cal.

Assuming $H' - H$ to be substantially constant between 100 to 130°C. , Eq. (5.38) integrates into

$$\log \frac{f_2}{f_1} = \frac{H' - H}{4.575} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

$$\log \frac{f_2}{f_1} = \frac{1,282}{4.575} \frac{(30)}{(373)(403)} = 0.0561,$$

therefore,

$$f_{130} = (1.137)(125) = 142 \text{ atm. and } \gamma_{130} = 0.710.$$

Dividing both sides of Eq. (5.39) by the absolute temperature and introducing the reduced pressure and reduced temperature give the following equation for the heat of vaporization into vacuum:

$$\frac{H' - H}{T} = \frac{-9RP_r}{128T_r} \left(1 - \frac{18}{T_r^2} \right). \quad (5.40)$$

Here again, as in the case of Eq. (5.23) for activity coefficients, it will be noticed that the so-called ideal heat of vaporization divided by the absolute temperature is a universal function of the reduced pressure and temperature and independent of the nature of the gas. Graphs of $(H' - H)/T$, as a function of the reduced pressure for various values of the reduced temperature, have been prepared,⁵ based on the same data used in constructing the universal activity coefficient curves. These curves may be used for rapidly estimating a useful approximate value for $H' - H$ for almost any gas over a wide range of conditions.

7. Equilibriums Involving Solutions and the Activity.—The conditions for equilibrium between solutions and the pure solid, liquid, or vapor components in equilibrium with the solution are essentially the same as the relations given above, with the exception that partial molar quantities must be substituted for the components of liquid or solid solutions. Thus, if a solution of sodium chloride is in equilibrium with ice and solid NaCl at the eutectic temperature, the following equilibrium conditions apply:

$$F_1 = \bar{F}_1 \quad F_2 = \bar{F}_2,$$

where F_1 and F_1 represent the molar free energy and partial molar free energy of the ice and water in solution, respectively, and F_2 and \bar{F}_2 are the molar free energy and partial molar free energy of the solid NaCl and dissolved NaCl respectively.

The equations for the dependence of partial molar free energies on temperature and pressure are derived in a manner similar to Eqs. (5.6) and (5.10), giving

$$\left(\frac{\partial \bar{F}_1}{\partial P}\right)_{T,N} = \bar{V}_1, \quad (5.41)$$

where \bar{V}_1 represents the partial molar volume of component 1, and the partial derivative is to be taken at constant temperature and composition. The change of partial molar free energy with temperature at constant pressure and composition is expressed by the equation

$$\left(\frac{\partial \bar{F}_1}{\partial T}\right)_{P,N} = -\bar{S}_1 = \frac{\bar{F}_1 - \bar{H}_1}{T}, \quad (5.42)$$

where \bar{S}_1 and \bar{H}_1 are the partial molar entropy and partial molar heat content of component 1, respectively.

The fugacity of a constituent in solution is defined analogously to that of a pure substance; thus

$$\bar{F}_1 = RT \ln f_1 + B_1. \quad (5.43)$$

The changes of fugacity of a dissolved constituent with respect to pressure and temperature are given by the equations

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_{T,N} = \frac{\bar{V}_1}{RT} \quad (5.44)$$

$$\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,N} = \frac{H_1' - \bar{H}_1}{RT^2}, \quad (5.45)$$

where $H_1' - \bar{H}_1$ is the heat absorbed, when 1 mole of constituent 1 vaporizes from such a large volume of solution that the composition does not change appreciably into a vacuum. This quantity is the so-called "ideal" heat of vaporization.

A quantity that has been found convenient in dealing with problems involving liquid and solid solutions is defined by the equation

$$a = \frac{f}{f^\circ}, \quad (5.46)$$

and is called the "activity." Since f° is a constant representing the fugacity of the pure substance in some reference state chosen as the standard state, the activity is always proportional to the fugacity. As a general rule, the standard state for pure gases is the state of unit fugacity, which is practically indistinguishable from the gas at 1 atm. pressure. Consequently, when dealing with gases, $a = f$; either term can be used interchangeably, although it is customary to speak of the fugacity of gases and activities of the components of liquid and solid solutions.

From Eq. (5.14) the free-energy change, accompanying the transfer of 1 mole of the substance from the standard state to one in which its fugacity is f , is given by the relation

$$F - F^\circ = RT \ln \frac{f}{f^\circ} = RT \ln a \quad (5.47)$$

or

$$a = e^{(F - F^\circ)/RT}. \quad (5.48)$$

Thus, the activity is a numerical measure of the free energy of transfer of 1 mole of the substance from its standard state to the equilibrium system under discussion, and is a more convenient quantity for dealing with equilibrium problems than free energies. This point will become clearer as applications to concrete problems are developed, when it will be found that the activity, and not the concentration in stoichiometric units, is a measure of the effective contribution of a substance in establishing equilibria involving chemical changes, distribution between phases, electromotive forces, etc.

Whenever measurements are made on systems involving solutions at equilibrium by an instrument, such as the potentiometer, in which the observed electromotive force is determined by the molar or partial molar free energies of the substances contributing to the equilibrium state, it will be seen (Chap. VI) that the electromotive force is related in a definite manner to the activities of these constituents; but the relation between the activity and concentrations expressed by any of the usual means must be determined by actual chemical analyses on the equilibrium system. In a few simple cases it is possible to eliminate the chemical analysis and transcribe the activities directly into stoichiometric units. The factor relating the concentration of a component to its activity is called the "activity coefficient."

The numerical value of the activity coefficient will depend on the concentration units employed and the choice of standard state (L-R, pp. 256-277). For nonaqueous solutions the standard states of solute and solvent are usually chosen so that in the infinitely dilute solution the activity of each component becomes equal to its mole fraction, and the activity coefficient approaches unity. A convenient measure of the activity of a solvent possessing a measurable vapor pressure in solution is the ratio of the vapor pressure of the solvent from solution to its vapor pressure in the pure state.

Since concentrations in aqueous solutions are customarily expressed as moles per 1,000 grams of water, the standard state of the solute is chosen so that the activity equals the molality in the infinitely dilute solution, and the activity coefficient equals unity. It is worth remembering that the standard state of solutes in aqueous solutions is a hypothetical state, in which the activity is unity and the partial molar volume, partial molar-heat content, and partial molar-heat capacity are those of the solute at infinite dilution. Although the choice of standard states may seem to be entirely arbitrary, it will be noted that in the infinitely dilute solutions they do break down into the so-called "laws" of perfect solutions and relate the fugacity of each component to their respective stoichiometric concentrations.

In the case of strong electrolytes the following conventions have been adopted:

For an acid, salt, or base which may be assumed completely ionized in accordance with the equation

$$x = \nu_+ x^+ + \nu_- x^-, \quad (5.49)$$

where ν_+ = moles, positive ions produced per mole of x ,

ν_- = moles, negative ions produced per mole of x ,

the measured activity, a , of x is related to the activities of the individual ions by means of the equation

$$a = (a_+^{\nu_+})(a_-^{\nu_-}). \quad (5.50)$$

Since no wholly acceptable procedure has been devised for measuring the activities of the individual ions, the geometrical mean of the ion activities is computed from the equation

$$a_{\pm} = a^{1/(\nu_+ + \nu_-)} = a^{1/\nu}. \quad (5.51)$$

In order to evaluate a mean ion activity coefficient, the mean molality is defined in terms of the molality of x by the equation

$$m_{\pm} = m(\nu_+^{\nu} \nu_-^{\nu})^{1/\nu}, \quad (5.52)$$

and consequently the mean ion activity coefficient equals

$$\gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}}. \quad (5.53)$$

Both the mean activity coefficient and mean molality are defined so that the activity of x is given by the expression

$$a = (\gamma_{\pm} m_{\pm})^{\nu}. \quad (5.54)$$

When a is determined by some equilibrium measurement, then a_{\pm} is computed from Eq. (5.51), the mean molality m is computed from Eq. (5.52), and the chemical analysis for m and γ_{\pm} is computed from Eq. (5.53). It is this value of the activity coefficient of an electrolyte that is recorded in tabulations of activity coefficients of electrolytes found in the literature. The activity coefficient has the particular properties that (1) in the absence of data on the temperature coefficient it may, as a first approximation, be assumed independent of temperature for moderate temperature variations; (2) it varies quite markedly with the concentration of the electrolytes in solution and is roughly the same in all solutions of the same ionic strength. The ionic strength μ is defined by the summation equation:

$$\mu = \frac{1}{2} \sum m_i z_i^2, \quad (5.55)$$

where m_i represents the molality of the i th ion, and z_i its valence.

The details of the various methods employed for the determination of activities are presented in Lewis and Randall (L-R, Chaps. XXII, XXIII, XXVI, and XXVII) in considerable detail and are listed here merely as a matter of review:

1. Vapor-pressure measurements.
2. Electromotive-force measurements.
3. Distribution-ratio method.
4. Solubility method.
5. Freezing-point method.
6. Boiling-point method.

In addition, it is possible to compute activity coefficients in dilute solutions by means of the equations developed in the

Debye-Hückel theory of electrolytes.^{6;7, Chap. 7} Thus, the activity coefficient of the ion constituent i is given by the equation

$$-\log \gamma_i = \frac{z_i^2 A \sqrt{\mu}}{1 + Ba_i \sqrt{\mu}}; \quad (5.56)$$

and the mean ion activity coefficient γ_{\pm} of a binary electrolyte is expressed by the equation

$$-\log \gamma_{\pm} = \frac{z_+ z_- A \sqrt{\mu}}{1 + Ba_i \sqrt{\mu}}. \quad (5.57)$$

In the above equation the log term refers to the base 10, A and B are constants for aqueous solutions at a given temperature, and a_i is an average effective diameter of all the ions in solution. It is of the order of several angstroms ($2 - 5 \times 10^{-8}$ cm.) and is usually obtained from the experimentally determined activity coefficients. The constants A and B have the following values in aqueous solutions:

| Temperature, °C. | A | $B \times 10^{-8}$ |
|------------------|--------|--------------------|
| 18 | 0.4992 | 0.3272 |
| 25 | 0.5056 | 0.3286 |
| 38 | 0.5186 | 0.3314 |

With a good guess for the value of a_i , Eqs. (5.56) and (5.57) hold quite well for uni-univalent electrolytes up to concentrations of 0.10 mole per liter and for bi-univalent electrolytes, up to about 0.05 mole per liter. Although Lewis and Randall have defined the ionic strength on the basis of concentrations expressed as molalities, and the Debye equations employ concentrations on a mole per unit volume basis, either system can be used in the dilute region where these relations are applicable.

Debye has also devised a theory for predicting activity coefficients of nonelectrolytes dissolved in solutions of electrolytes. For solutions of moderate ionic strengths the equation derived for computing the activity coefficient of the nonelectrolyte is

$$\log \gamma = k\mu, \quad (5.58)$$

where the constant k depends on the nature of the ions in solution, as well as the nonelectrolyte, and must be determined by experi-

ment. The chief point of interest in this equation is that the activity coefficient, and hence the escaping tendency of the non-electrolyte, must increase with increasing ionic strength or, in other words, the solubility should be decreased by the ions present.

Since the activity is proportional to the fugacity, it follows that

$$d \ln f = d \ln a, \quad (5.59)$$

and consequently the differential equations expressing the dependence of activity on temperature and pressure are identical with those derived for fugacities (5.44) and (5.45).

One additional important relation is required in order to round out the basic theory for the use of fugacities and activities, *i.e.*, the dependence of these quantities on changes of composition at constant temperature and pressure. The fundamental equation of partial molar quantities may be expressed in the form [Eq. (3.30)]

$$\sum n_i d\bar{G}_i = 0, \quad (5.60)$$

where \bar{G}_i is any partial molar property of the i th component and n_i is the corresponding number of moles of the i th component. In this case the partial molar property of interest is the partial molar free energy, which is related to the fugacity and activity by means of Eqs. (5.43) and (5.47), and therefore

$$d\bar{F}_i = RTd \ln f_i = RTd \ln a_i. \quad (5.61)$$

Substituting in (5.60) gives the following equations for computing the changes in fugacity and activity, with composition at constant temperature and pressure:

$$n_1 d \ln f_1 + n_2 d \ln f_2 + \cdots = 0, \quad (5.62)$$

$$n_1 d \ln a_1 + n_2 d \ln a_2 + \cdots = 0. \quad (5.63)$$

These equations cannot be integrated directly, since no general algebraic relations exist between composition and escaping tendencies, which would permit analytical integration. Graphical integration of these equations is frequently employed, however, to compute the activity of one component of a binary system, where the activity of the first component may be determined by vapor-pressure measurements, freezing-point determinations, etc.

When the system under consideration contains n components, it is necessary to measure the activities of $n-1$ components over a range of concentrations in order to obtain the activities of the n th component over the same range. Thus, if the activities of NaOH, NaCl, and H_2O are required in a series of solutions of these three substances, it would be possible to determine the activity of the H_2O by measuring its vapor pressure; the activity of the NaOH could be determined by suitable electromotive-force measurements; and the corresponding NaCl activities could be computed by graphical integration of the equation

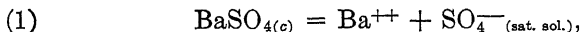
$$- \int m_3 d \ln a_3 = \int 55.51 d \ln a_1 + \int m_2 d \ln a_2, \quad (5.64)$$

in which m_2 and m_3 represent the molalities of the NaOH and NaCl, respectively. Unfortunately, the technique of extrapolating these integrals to infinite dilution has not been developed to the same useful extent as in the case of binary solutions; consequently, this procedure is rarely used on systems containing more than two components.

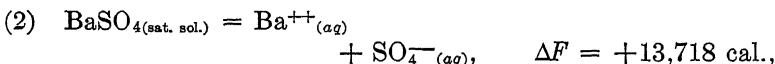
8. Calculation of Solubilities from Free Energies of Solution.

Illustration 3.—The free energy of solution of 1 mole of $BaSO_4$ in water is +13,718 cal. Calculate: (a) the solubility of $BaSO_4$ in pure water at $25^\circ C.$, assuming the activity coefficient to be unity; (b) the solubility based on a mean activity coefficient calculated from the Debye equation (5.57).

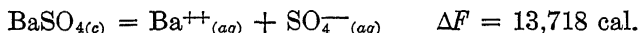
Solution.—a. For the transfer process indicated by the equation



$\Delta F = 0$, since the solid is in equilibrium with the saturated solution; and for the transfer,



where the subscript (aq) indicates $BaSO_4$ in a solution of unit activity. Consequently the free energy of solution corresponds to the transfer



which, from Eq. (5.47) defining activity, can be expressed as

$$\Delta F = RT \ln \frac{a_1}{a_{sat. sol.}}$$

where a_1 = activity of BaSO_4 in the state of unit activity = 1.

$a_{\text{sat. sol.}}$ = activity of BaSO_4 in the saturated solution, which from Eqs. (5.52)–(5.54) equals $(\gamma_{\pm} m_{\pm})^2$.

Assuming $\gamma_{\pm} = 1$, $a_{\text{sat. sol.}} = m_{\pm}^2 = m^2$, since in this case the molality and mean molality are the same. Therefore

$$\Delta F = 13,718 = (4.575)(298.1) \log \frac{1}{m^2},$$

or

$$-\log m = \frac{13,718}{(4.575)(298.1)(2)} = 5.028.$$

Therefore

$$m = 9.38 \times 10^{-6} \text{ mole BaSO}_4 \text{ per kilogram H}_2\text{O}.$$

b. In order to estimate the activity coefficient in a saturated solution of BaSO_4 , the ionic strength is first computed [Eq. (5.55)]

$$\mu = \frac{1}{2}[9.3 \times 10^{-6}(4) + 9.3 \times 10^{-6}(4)] = 37.2 \times 10^{-6}.$$

Substituting

$$A = 0.5056$$

$$B = 0.3286 \times 10^8$$

in Eq. 5.57 and estimating $a_i = 4 \times 10^{-8}$ cm. give

$$-\log \gamma_{\pm} = \frac{(4)(0.5056) \sqrt{37.2 \times 10^{-6}}}{1 + 0.3286(4) \sqrt{37.2 \times 10^{-6}}} = 0.0122.$$

Therefore

$$\gamma_{\pm} = 0.972.$$

Consequently

$$a_{\text{sat. sol.}} = m^2(0.972)^2.$$

Therefore

$$-\log 0.972m = 5.028$$

$$m = \frac{9.38 \times 10^{-6}}{0.972} = 9.65$$

$$\times 10^{-6} \text{ mole BaSO}_4 \text{ per liter.}$$

Within the accuracy with which solubilities of highly insoluble compounds are known, it makes little difference whether molalities or activities are employed. It is interesting to note, however, that even in a solution as dilute as $10^{-5}m$, activity coefficients of bi-bivalent compounds are noticeably less than unity. In the use of free-energy data to evaluate solubilities, it is

important that solubilities be expressed as stoichiometric molalities and not as mean molalities. Thus, if m_{\pm} computed for $\text{Ca}(\text{OH})_2$ were 2×10^{-2} , the stoichiometric molality (5.52) would be 1.26×10^{-2} mole per 1,000 grams H_2O .

9. Evaluation of Enthalpy Changes Accompanying Vaporization and Fusion from Change of Escaping Tendencies with Temperature.—Equations (5.28), (5.30), (5.38), and (5.45) may readily be integrated for computing the change of escaping tendency with temperature, provided that the requisite enthalpy data are available. Quite frequently the process is reversed, and ΔH is computed from the observed change of vapor pressure, fugacity, or activity with temperature.

Either Eq. (5.28) or (5.30) may be used to compute heats of vaporization if the vapor is at such pressures that deviations from ideality are not too serious. Strictly speaking, Eq. (5.29) should be applied when the vapor-pressure data have been obtained by the static method over liquids under their own saturation pressures; Eq. (5.31) should be used when the vapor pressures have been obtained by the dynamic method under a constant total pressure. As pointed out in Sec. 5, the two ΔH 's are somewhat different in a physical sense, but the numerical difference is generally less than the accuracy of the calculations as a whole.

10. Calculation of ΔH of Vaporization from Vapor Pressures.

Illustration 4.—The heat of vaporization of $\text{HNO}_{3(l)}$ has been indirectly evaluated from heat of solution data by Berthelot to be 7,260 cal./mole at 18°C . (B-R). On the basis of the following measured vapor pressures⁸ of 100 per cent nitric acid, derive an independent value for the heat of vaporization:

| | | | |
|-------------------------------------|------|------|------|
| Temperature, $^\circ\text{C}$ | 0 | 12.5 | 25.0 |
| Vapor pressure (mm. Hg)..... | 15.9 | 31.5 | 62.1 |

Solution.—For the transformation



Eq. (5.29)

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$$

may be integrated by expressing ΔH as a function of temperature by means of the equation

$$\frac{d\Delta H}{dT} = \Delta C_p.$$

The I.C.T. value for the heat capacity of liquid HNO_3 is 29 cal./mole, and the heat capacity of gaseous HNO_3 is estimated to be 12 cal.; hence ΔC_p is -17 and

$$\Delta H = \Delta H_0 - 17T.$$

Substituting this expression in Eq. (5.29) and integrating give

$$R \ln p + 17 \ln T = I - \frac{\Delta H_0}{T} = \Sigma.$$

Three values for Σ are then computed from the equation

$$\Sigma = 4.575 \log p + 39.15 \log T,$$

by substituting the foregoing vapor pressures and temperatures. ΔH may then be obtained from the slope of the $\Sigma - 1/T$ plot or by algebraic solution of the three Σ equations. The average value for ΔH_0 obtained by this method is 14,080, and from the equation

$$\Delta H = 14,080 - 17T,$$

the heat of vaporization at 18°C . is found to be 9,130 cal./mole. The heat of vaporization at the normal boiling point (359°K .), computed from this equation, is 7,980 cal., which is equivalent to a Trouton's constant of 22.2. Since the HONO_2 molecules in the liquid state probably undergo a certain amount of hydrogen bonding, a high Trouton's constant, rather than a low value, is to be expected.

The foregoing evaluation of ΔH has been based on vapor-pressure data obtained by the static method between 0.021 and 0.082 atm. pressure of HNO_3 , and, strictly speaking, is not identical with the ΔH of vaporization at 1 atm. Furthermore, in accordance with the discussion in Chap. II, Sec. 11, the equation

$$\frac{d\Delta H}{dT} = \Delta C_p$$

is only approximately correct for calculating the temperature coefficient of heats of vaporization, and the assumption of ideal gas behavior for HNO_3 is probably quite bad. Consequently the calculated value for the heat of vaporization of pure HNO_3 is

only an approximate value, but is probably better than the value 7,260 cal. at 18°C., which when corrected to the normal boiling point would give a Trouton's constant of about 17.

Heats of fusion may be deduced from data on the temperature variation of liquid-solid equilibria in binary systems, where the composition of the two phases in equilibrium has been established. The procedure is straightforward for those systems in which the solid phase is either a pure solid or solid solution of the two components. Consider the case in which pure 1 crystallizes from a solution of 1 and 2 under equilibrium conditions. The partial molar free energy, \bar{F}_1 of 1, in the solution, referred to pure liquid 1 as the reference state, is

$$\bar{F}_1 - F_1^\circ = RT \ln a_1 = RT \ln \gamma_1 N_1, \quad (5.65)$$

where F_1° equals the molar free energy of pure liquid 1, N_1 represents the mole fraction of 1 in solution, and γ_1 is the corresponding activity coefficient. Since the system is in equilibrium

$$\bar{F}_1 = F_{1-s}^\circ, \quad (5.66)$$

where F_{1-s}° represents the constant molar free energy of pure, solid 1 at the temperature T of the system. Substituting the value of \bar{F}_1 from Eq. (5.65) in (5.66) gives

$$F_{1-s}^\circ = F_1^\circ + RT \ln \gamma_1 N_1 \quad (5.67)$$

or

$$F_1^\circ - F_{1-s}^\circ = -RT \ln \gamma_1 N_1. \quad (5.68)$$

In this equation $F_1^\circ - F_{1-s}^\circ$ represents the molar free energy of pure liquid 1, minus the molar free energy of solid 1; and the corresponding enthalpy change is the molar-heat content of the liquid, less the molar-heat content of the solid; in other words, ΔH_1 , the heat of fusion of component 1. Consequently Eq. (5.12) may be used to compute the change of $\ln a_1$ with temperature by substituting the heat of fusion ΔH_1 for the ΔH term in this equation. Equation (5.12) becomes

$$\left[\frac{\partial (\ln \gamma_1 N_1)}{\partial T} \right]_P = \frac{\Delta H_1}{RT^2} \quad (5.69)$$

or

$$-\frac{\Delta H_1}{R} = \left(\frac{\partial \ln \gamma_1 N_1}{\partial \frac{1}{T}} \right)_P. \quad (5.70)$$

Thus, the slope of the $\log \gamma_1 N_1$ vs. $1/T$ plot multiplied by 4.575 equals the heat of fusion of component 1.

When the solid phase in equilibrium with the binary solution is a solid solution of the two components, the conditions for equilibrium can be written:

$$\bar{F}_1 = \bar{F}'_{1(\text{s.s.})} \quad (5.71)$$

$$\bar{F}_2 = \bar{F}'_{2(\text{s.s.})} \quad (5.72)$$

where the unprimed symbols refer to the liquid phase and the primed, to the solid-solution phase. Choosing the pure liquid and pure solid components as the reference states for the liquid and solid phases, respectively, leads to the equations

$$F_1^\circ + RT \ln \gamma_1 N_1 = F_1^{\circ'} + RT \ln \gamma_1' N_1', \quad (5.73)$$

$$F_2^\circ + RT \ln \gamma_2 N_2 = F_2^{\circ'} + RT \ln \gamma_2' N_2'. \quad (5.74)$$

Therefore

$$F_1^\circ - F_1^{\circ'} = RT \ln \frac{\gamma_1' N_1'}{\gamma_1 N_1}. \quad (5.75)$$

$$F_2^\circ - F_2^{\circ'} = RT \ln \frac{\gamma_2' N_2'}{\gamma_2 N_2}. \quad (5.76)$$

Since in Eqs. (5.75) and (5.76) the free-energy differences represent the difference between the molar free energies in the pure liquid and solid states, it follows that the accompanying enthalpy changes are the heats of fusion of the pure substances. Hence the temperature coefficients of Eqs. (5.75) and (5.76) are

$$\left(\frac{\partial \ln \frac{\gamma_1' N_1'}{\gamma_1 N_1}}{\partial T} \right)_P = -\frac{\Delta H_1}{RT^2}, \quad (5.77)$$

$$\left(\frac{\partial \ln \frac{\gamma_2' N_2'}{\gamma_2 N_2}}{\partial T} \right)_P = -\frac{\Delta H_2}{RT^2}. \quad (5.78)$$

Consequently,

$$\frac{\Delta H_1}{R} = \left(\frac{\partial \ln \frac{\gamma_1' N_1'}{\gamma_1 N_1}}{\partial \frac{1}{T}} \right)_P, \quad (5.79)$$

and a similar equation applies for ΔH_2 . Hence the heat of fusion equals 4.575 times the slope of the $\log \gamma_1' N_1' / \gamma_1 N_1$ vs. $1/T$ plot.

In view of the paucity of data on activity coefficients in all but aqueous systems, it is customary in applying these equations to assume that the activity coefficients equal unity and to employ this procedure on dilute solutions. An excellent summary of this branch of thermochemistry applied to inorganic substances has been prepared by Kelley.⁹

11. Estimation of ΔH of Fusion from Melting Point-composition Data. *Illustration 5.*—Morey and Bowen¹⁰ report the following melting points in the system $\text{Na}_2\text{SiO}_3\text{-SiO}_2$:

| Temperature, °K. | $1000/T$ | Mole, per cent Na_2SiO_3 |
|------------------|----------|--|
| 1361.1 | 0.7347 | 100.00 |
| 1359.6 | 0.7355 | 99.23 |
| 1304.1 | 0.7668 | 82.32 |
| 1274.1 | 0.7849 | 79.27 |
| 1136.1 | 0.8802 | 63.42 |

Estimate the molar heat of fusion of Na_2SiO_3 and the entropy of fusion at the melting point from these data.

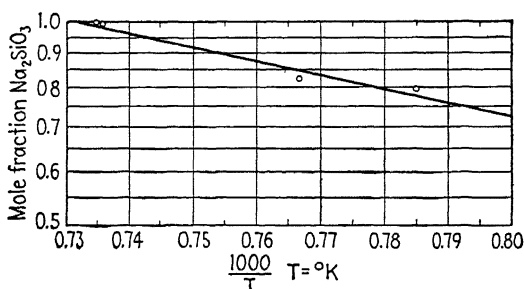


Fig. 6.—Melting points in the system $\text{Na}_2\text{SiO}_3\text{-SiO}_2$.

Solution.—Since the solid phase in equilibrium with the solutions of the indicated compositions is known to be Na_2SiO_3 and not a solid solution or other complex phase, Eq. (5.70) may be employed. In order to minimize the error introduced by the assumption of unit activity coefficients and constant heat of fusion, only the first four points in the dilute SiO_2 region will be employed.

These data are presented in the form of a $\log N - 1/T$ plot on Fig. 6. It will be noticed that the experimental points deviate appreciably from the straight line, as drawn, indicating no great accuracy for the heat of fusion obtained from these data. The estimated heat of fusion read from the plot is 10,100 cal. The entropy of fusion at the melting point is

$$\frac{10,100}{1,361} = 7.4 \text{ E.U.}$$

Although experimental errors undoubtedly account for some of the deviations of the individual points from the straight line, it is more likely in this case that the activity coefficients of the silicate differ appreciably from unity due to various types of intermolecular or interionic forces in the molten solution of the two components. Since the change of heat of fusion between these extremes of temperatures is certainly less than 1,000 cal., the uncertainty introduced by neglect of this factor is negligible.

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CHAPTER VI

EQUILIBRIUMS IN CHEMICAL PROCESSES AND THE FREE-ENERGY CHANGE

1. The Third Law of Thermodynamics.—Before we proceed with the subject of the evaluation of free-energy changes accompanying chemical reactions, a brief discussion of the third law of thermodynamics is essential. The free-energy change corresponding to the process under consideration may be computed from Eq. (1.9), defining the free-energy change, namely,

$$\Delta F = \Delta H - T\Delta S. \quad (6.1)$$

Methods have been discussed for computing the enthalpy change accompanying a given physical or chemical transformation under any conditions of temperature or pressure of interest, provided the requisite fundamental data are available. The problem is, therefore, to compute the ΔS term in Eq. (6.1) in order to solve for ΔF . Although several other methods will be discussed for evaluating ΔF , the method based on the direct use of this equation will be found to offer the most extensive and perhaps the most accurate possibilities for applications in all branches of chemistry.

From the definition of the entropy change accompanying a reversible process [Eq. (1.5)], it follows that the entropy change, experienced by a substance when heated from T_1 to T_2 at constant pressure, is

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_p dT}{T} \quad (6.2)$$

If, for example, it is possible to express C_p as a function of temperature in the range of interest by means of Eq. (2.11), integration of (6.2) gives

$$S_2 - S_1 = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2} (T_2^{-2} - T_1^{-2}) \quad (6.3)$$

for the entropy change accompanying the heating of a pure substance from T_1 to T_2 in the absence of changes of state or

crystallographic transitions. If any of these changes occur between the temperatures of interest, it is necessary to add the term

$$\sum \frac{\Delta H_i}{T_i} \quad (6.4)$$

where ΔH_i represents the increase in enthalpy occurring at the temperature at which the two phases are in equilibrium (T_i), due allowance being made for the difference in heat capacities of the various phases encountered in passing from T_1 to T_2 . Thus it is possible to compute the entropies of pure substances relative to some definite temperature if the necessary heat capacity and heat of transition data are available. If the absolute zero is chosen as the reference temperature, the entropy at the temperature T is then

$$S_T - S_0 = \int_0^T \frac{C_p dT}{T} + \sum \frac{\Delta H_i}{T_i} \quad (6.5)$$

In accordance with the third law, *the entropy at the absolute zero of temperature of any phase of sharply specifiable energy is zero*; consequently

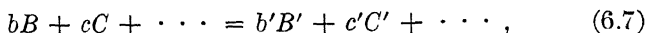
$$S_0 = 0 \quad (6.6)$$

in Eq. (6.5). The reason for the qualifying phrase "sharply specifiable energy" will be discussed in Chap. VII along with certain apparent contradictions to the law, after a brief discussion of the statistical calculations of entropies has been presented.

Thus by suitable extrapolation of the heat capacities of the elements and pure compounds measured from room temperature down to some low temperature near the melting point of H_2 ($15^\circ K.$) or the boiling point of O_2 ($90^\circ K.$), it is possible to build up a table of standard entropies of all known pure substances, which may then be used to calculate the ΔS of any desired chemical reaction. The ΔS for any process is computed by subtracting the sum of the entropies of the substances constituting the initial state of the system from the sum of the entropies of the substances in the final state, at the temperature in question. Since at low temperatures heat capacities vary quite rapidly with temperature and approach zero with approach to the absolute zero, it is necessary to resort to graphical integration of Eq. (6.5). Methods for performing this integration are

described in detail in Lewis and Randall and Parks and Huffman,¹ and are discussed in Chap. VII, in connection with the use of Debye specific heat functions for performing the extrapolation to 0°K.

2. The Equilibrium Constant and the Standard Free-energy Change.—Consider the chemical change of state represented by the equation



where the capital letters designate species, the small letters the number of moles of each species involved, and the primed letters refer to the products formed. Let the activities in the actual initial and final states be $a_B, a_C, \dots, a_{B'}, a_{C'}, \dots$; then from the definition of activity (5.47) it follows that the difference between the molar free energy of each substance in the actual system and in some convenient reference state chosen as the standard state is

$$\begin{aligned} F_B - F_B^\circ &= RT \ln a_B, \\ F_C - F_C^\circ &= RT \ln a_C, \text{ etc.} \end{aligned}$$

Therefore the molar free energies in the actual system are

$$F_B = RT \ln a_B + F_B^\circ, \quad (6.8)$$

$$F_C = RT \ln a_C + F_C^\circ, \text{ etc.}, \quad (6.9)$$

or for the actual number of moles of each substance involved

$$bF_B = RT \ln a_B^b + bF_B^\circ, \quad (6.10)$$

$$cF_C = RT \ln a_C^c + cF_C^\circ, \text{ etc.} \quad (6.11)$$

The corresponding free-energy change for the actual process is

$$\Delta F = b'F_{B'} + c'F_{C'} + \cdots - (bF_B + cF_C + \cdots). \quad (6.12)$$

Substituting Eqs. (6.10) and (6.11) in (6.12) gives

$$\begin{aligned} \Delta F = RT \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots} + b'F_{B'}^\circ + c'F_{C'}^\circ + \cdots \\ - (bF_B^\circ + cF_C^\circ + \cdots). \end{aligned}$$

Therefore

$$\Delta F = RT \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots} + \Delta F^\circ. \quad (6.13)$$

If now the transformation represented by Eq. (6.7) is visualized to take place when the system is at equilibrium, $\Delta F = 0$, and therefore

$$-\Delta F^\circ = RT \ln \frac{a_{B^{b'}} \cdot a_{C^{c'}} \cdot \cdot \cdot}{a_B^b \cdot a_C^c \cdot \cdot \cdot} = RT \ln K, \quad (6.14)$$

where the activities are no longer general but refer to their value in the system at equilibrium, and ΔF° represents the free-energy change corresponding to the production of the indicated number of moles of B' , C' , $\cdot \cdot \cdot$ in their standard states (state of unit activity) from b moles of B , c moles of C , etc., in their standard states.

There is a tendency among some students to overestimate the importance of the left-hand side of Eq. (6.14) and neglect its significance in terms of the equivalent numerical value of the equilibrium constant K . When, for example, the standard free-energy change of a given reaction at room temperature is of the order of $-50,000$ cal., there is little doubt that the reaction will go to completion within some reasonable range of temperatures, provided a catalyst may be found that will make the reaction go at a measurable rate. On the other hand, when the free-energy change is of the order of, say, $+6,000$ cal., there is a tendency to conclude that it is only necessary to "push" this much energy into the system in order to produce the number of moles indicated by the chemical equation from the corresponding moles of reactants. It is true that if the reaction were adaptable to being performed in an electrolytic cell, the minimum amount of electrical energy required for the production indicated by the chemical equation would be $6,000$ cal. or $25,000$ joules; but, unless the products of electrolysis were continuously withdrawn from the field of the reaction, the cell process would become extremely inefficient or cease altogether. However, since most reactions are not usually carried out in electrolytic cells but in ordinary reaction vessels, the significance of the $+6,000$ cal. resides in the equivalent numerical value of K , which determines the maximum conversions obtainable in the reaction system with all the indicated components present. If one (or more) of the products escapes from the reaction zone as a vapor or precipitated solid, the reaction then goes to completion; but this fact is known in a qualitative way from Le Chatelier's principle without recourse to

free energy. In such cases the total enthalpy changes involved are important, since these data determine the amount of heat that must be supplied to the reaction system in order to make the reaction go and maintain temperatures that give practical rates of reaction.

Another regrettable tendency is to condemn a reaction as being unworkable simply on the basis of a moderately positive free-energy change. Here again, the actual equilibrium constant should be evaluated over a series of temperatures, and the maximum conversions attainable computed for a range of concentrations and pressures.

3. Dependence of Equilibrium Conversion on Reaction Type.

Illustration 1.—In order to demonstrate more definitely the numerical significance of a positive free-energy change, consider the following three types of gas phase reactions at a constant pressure of 1 atm.:

- | | |
|-----|---------------|
| (1) | $A + B = C,$ |
| (2) | $A + B = 2C,$ |
| (3) | $A + B = 3C.$ |

In the first reaction a contraction in volume occurs, in the second no change of volume occurs, and in the third case an increase in volume occurs. Assuming that the standard free-energy change for all three reactions at 300°C. is +2,620 cal., compute the mole per cent conversion of A or B attainable at equilibrium when starting with an initially equimolar mixture of A and B .

Solution.—Since $\Delta F^\circ_{573} = 2,620$ cal.,

$$-2,620 = RT \ln K = 4.575(573) \log K;$$

therefore

$$K = 10^{-1}.$$

Case 1. $A + B = C.$

If $n_A = n_B = n$ = initial moles of A or B and $100x$ = mole per cent of A or B converted at equilibrium,

$$\Sigma \text{ moles at equilibrium} = 2n(1 - x) + nx = n(2 - x).$$

Therefore

$$P_A = P_B = \frac{n(1 - x)}{n(2 - x)} \quad P_C = \frac{nx}{n(2 - x)}.$$

Therefore

$$K_1 = \frac{x(2-x)}{(1-x)^2} = 0.1 \text{ and solving gives } x = 0.046.$$

Case 2. $A + B = 2C$.

In this case,

$$K_2 = \frac{4x^2}{(1-x)^2} = 0.1 \quad \text{and} \quad x = 0.136.$$

Case 3. $A + B = 3C$.

In this case Σ moles at equilibrium $= n(2+x)$

$$P_A = P_B = \frac{(1-x)}{2+x} \quad P_c = \frac{3x}{2+x}.$$

Therefore

$$K_3 = \frac{27x^3}{(2+x)(1-x)^2} = 0.1 \quad \text{and} \quad x = 0.18.$$

Thus it will be noted that, although in the first case the maximum conversion attainable for the specified concentrations would only be 4.6 per cent, in the second and third cases the conversions would be 13.6 and 18 per cent, respectively. Furthermore, since the first reaction occurs with a contraction in volume, pressure would have an advantageous effect on this equilibrium. These calculations emphasize the necessity for actually computing some equilibrium conversions before rejecting a reaction as being economically unattractive, merely on the basis of a moderately positive standard free-energy change. A number of profitable industrial processes are known that operate on smaller conversions than 15 per cent.

4. The Change of the Equilibrium Constant with Temperature.

By deducting the sum of the coefficients representing the change of standard free energies with temperature from the corresponding sum for the products of the reaction, the following equation is obtained for the temperature dependence of the standard free-energy change of a chemical reaction [see Eq. (5.11)]:

$$\left(\frac{\partial \Delta F^\circ}{\partial T} \right)_P = \frac{\Delta F^\circ - \Delta H}{T} \quad (6.15)$$

or, in the more familiar form,

$$d \left(\frac{\Delta F^\circ}{T} \right) = - \frac{\Delta H}{T^2} dT. \quad (6.16)$$

Substituting $\Delta F^\circ = -RT \ln K$ in Eq. (6.16) gives

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}. \quad (6.17)$$

From this equation it will be seen that the direction in which an equilibrium is shifted by temperature depends solely on the enthalpy change of the reaction and not the entropy change. If ΔH is positive (endothermic reaction), K increases with increasing temperature; whereas, if heat is liberated by the process, K decreases with increasing temperature, and the maximum theoretical conversions obtainable at equilibrium decrease. The possibility of ΔH changing sign with temperature should not, however, be overlooked.

When the temperature range of interest is small or the accuracy of the enthalpy data does not warrant the formulation of ΔH as a function of temperature, Eq. (6.17) is integrated on the assumption that ΔH is constant, giving

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{4.575} \left(\frac{T_2 - T_1}{T_2 T_1} \right). \quad (6.18)$$

In the general case, ΔH is expressed as a function of temperature by means of Eq. (4.7) or (4.8), depending on the heat-capacity function employed. Thus, substituting Eq. (4.7) in (6.17) gives

$$\frac{d \ln K}{dT} = \frac{\Delta H_0 + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3}{RT^2}. \quad (6.19)$$

which when integrated and rearranged yields

$$R \ln K - \Delta a \ln T - \frac{\Delta b}{2} T - \frac{\Delta c}{6} T^2 = I - \frac{\Delta H_0}{T} = \sum, \quad (6.20)$$

where I equals a constant of integration. When heat capacities are expressed by means of equations of the form

$$C_p = a + bT - cT^{-2},$$

the equation corresponding to (6.20) is

$$R \ln K - \Delta a \ln T - \frac{\Delta b}{2} T + \frac{\Delta c}{2} T^{-2} = I - \frac{\Delta H_0}{T} = \sum. \quad (6.21)$$

In order to apply Eqs. (6.20) and (6.21), it is necessary to know (a) one or more values of K at definite temperatures, (b) the heat-capacity constants Δa , etc., and (c) the heat of the reaction at a definite temperature in order to determine ΔH_0 .

Since Eqs. (6.20) and (6.21) are perhaps the most important equations in the field of chemical thermodynamics from the chemist's viewpoint, and since methods for determining items (b) and (c) have already been discussed, it would appear pertinent at this point to summarize the different methods employed for evaluating the integration constants of these equations.

1. Direct experimental determination of K at a series of temperatures.

2. Measurements of the necessary enthalpy and entropy data required for use in conjunction with the equation

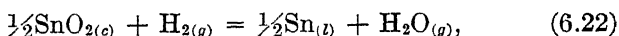
$$\Delta F^\circ = \Delta H - T\Delta S.$$

3. Calculation of the standard free-energy change corresponding to the reaction in question from the measured electromotive force of a suitable cell.

4. Computation of ΔF° for the reaction from standard free energies of formation of the substances involved, if already known.

5. Direct Measurements of Equilibrium Constants.—As an illustration of the method for determining the integration constant of the $\ln K - T$ equation from equilibrium data, the following example, based on the direct measurement of the equilibrium in the system $\text{SnO}_2 - \text{H}_2 - \text{Sn} - \text{H}_2\text{O}$, will be considered.

Illustration 2.—Emmett and Shultz² measured the equilibrium constant corresponding to the reaction



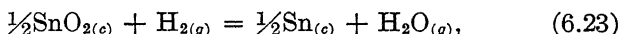
in a modified static system, which permitted recirculation of the gas phase over the solid phase until no further change in pressure was observed. Since the partial pressure of H_2O was maintained constant by passing the H_2 through a thermostatted water saturator at a definite temperature, it was only necessary to measure the total pressure on the system and deduct the H_2O pressure corresponding to the saturator temperature in order to obtain the partial pressure of hydrogen. These investigators

report the following values for the ratio $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ at the following temperatures:

| Temperature, °C. | $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ |
|------------------|---|
| 650 | 1.66 |
| 700 | 2.22 |
| 750 | 2.84 |
| 800 | 3.53 |

a. Derive an equation for the equilibrium constant for this reaction as a function of temperature of the form of Eq. (6.21).

b. Compute the standard free-energy and entropy changes for the reaction



at 25°C.

Solution.—a. With the standard states as indicated by Eq. (6.22), the equilibrium constant for this reaction is given by the equation

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \left(\frac{a_{\text{Sn}}}{a_{\text{SnO}_2}} \right)^{\frac{1}{2}}.$$

Since the authors record $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ as the equilibrium constant, the solubility of SnO_2 in liquid tin must be small enough so that the activity of the tin remains constant. The following calculations assume that such is the case.

Evaluation of ΔC_p for the reaction

$$\begin{aligned} \frac{1}{2}\text{SnO}_{2(c)} + \text{H}_{2(g)} &= \frac{1}{2}\text{Sn}_{(c)} + \text{H}_2\text{O}_{(g)}. \\ \frac{1}{2}\text{Sn}_{(c)} C_p &= 2.53 + 2.40 \times 10^{-3}T \\ \text{H}_2\text{O}_{(g)} C_p &= 7.00 + 2.77 \times 10^{-3}T \\ \text{Sum} &= 9.53 + 5.17 \times 10^{-3}T \\ \text{H}_{2(g)} C_p &= 6.62 + 0.81 \times 10^{-3}T \\ \frac{1}{2}\text{SnO}_{2(c)} C_p &= 6.97 + 2.83 \times 10^{-3}T - 1.26 \times 10^5 T^{-2} \\ \text{Sum} &= 13.59 + 3.64 \times 10^{-3}T - 1.26 \times 10^5 T^{-2} \end{aligned}$$

Therefore

$$\Delta C_p = -4.06 + 1.53 \times 10^{-3}T + 1.26 \times 10^5 T^{-2}. \quad (6.24)$$

Consequently ΔH for this reaction is

$$\Delta H = \Delta H_0 - 4.06T + 0.765 \times 10^{-3}T^2 - 1.26 \times 10^5 T^{-1}. \quad (6.25)$$

From Bichowsky and Rossini the following heats of formation at 18°C. are obtained:

$$\begin{aligned}\text{H}_2\text{O}_{(g)} \Delta H &= -57,801 \text{ cal.} \\ \frac{1}{2}\text{SnO}_{2(c)} \Delta H &= -69,050 \text{ cal.} \\ \Delta H [\text{reaction (6.23)}] &= 11,250 \text{ cal. at } 18^\circ\text{C.}\end{aligned}$$

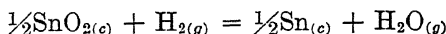
Substituting this value in Eq. (6.25) and solving for ΔH_0 yield

$$\Delta H = 12,800 - 4.06T + 0.765 \times 10^{-3}T^2 - 1.26 \times 10^5T^{-1}.$$

At the melting point of tin (504.9°K.) the heat of this reaction is

$$\Delta H = 10,700 \text{ cal.}$$

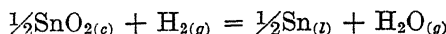
Consequently, adding reaction (6.23)



and

$$\frac{1}{2}\text{Sn}_{(c)} = \frac{1}{2}\text{Sn}_{(l)} \quad \Delta H = 860 \text{ cal.}$$

gives reaction (6.22)



for which

$$\Delta H_{504.9} = 10,700 + 860 = 11,560 \text{ cal.}$$

Since the heat capacity of liquid tin is different from the heat capacity of solid tin, a new heat-capacity function must be derived for reaction (6.22).

$$\begin{aligned}\frac{1}{2}\text{Sn}_{(l)} C_p &= 3.3 \\ \text{H}_2\text{O}_{(g)} C_p &= \frac{7.00 + 2.77 \times 10^{-3}T}{\text{Sum} = 10.3 + 2.77 \times 10^{-3}T} \\ \text{H}_{2(g)} C_p &= 6.62 + 0.81 \times 10^{-3}T \\ \frac{1}{2}\text{SnO}_{2(c)} C_p &= \frac{6.97 + 2.83 \times 10^{-3}T - 1.26 \times 10^5T^{-2}}{\text{Sum} = 13.59 + 3.64 \times 10^{-3}T - 1.26 \times 10^5T^{-2}} \\ \Delta C_p &= -3.29 - 0.87 \times 10^{-3}T + 1.26 \times 10^5T^{-2}. \quad (6.26)\end{aligned}$$

Therefore

$$\Delta H = \Delta H_0 - 3.29T - 0.435 \times 10^{-3}T^2 - 1.26 \times 10^5T^{-1}. \quad (6.27)$$

Substituting $\Delta H_{504.9}$ in Eq. (6.27) permits the determination of ΔH_0 and therefore

$$\begin{aligned}\Delta H &= 13,580 - 3.29T - 0.435 \times 10^{-3}T^2 \\ &\quad - 1.26 \times 10^5T^{-1}. \quad (6.28)\end{aligned}$$

From Eqs. (6.26) and (6.27) it will be seen that the constants to be substituted in the $\ln K - T$ equation have the following values:

$$\begin{aligned}\Delta a &= -3.29 & \Delta b &= -0.87 \times 10^{-3} & \Delta c &= -1.26 \times 10^5 \\ \Delta H_0 &= 13,580.\end{aligned}$$

Consequently

$$4.575 \log K + 7.57 \log T + 0.435 \times 10^{-3}T - 0.63 \times 10^5 T^{-2} + \frac{13,580}{T} = I. \quad (6.29)$$

Substituting the above values for $K = P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ in this equation gives the following computed values for I :

| Temperature, °K. | K^* | I |
|------------------|-------|-----------|
| 923.1 | 1.66 | 38.50 |
| 973.1 | 2.22 | 38.51 |
| 1023.1 | 2.84 | 38.49 |
| 1073.1 | 3.53 | 38.50 |
| | | Av. 38.50 |

Substituting the above average value for I in Eq. (6.29) and rearranging give the following required equation for computing the equilibrium constant of the reaction expressed by Eq. (6.22):

$$\log K = 8.415 - 1.66 \log T - 9.51 \times 10^{-5}T - 2968T^{-1} + 1.38 \times 10^4 T^{-2}. \quad (6.30)$$

b. In order to obtain the standard free-energy change for reaction (6.23) at 25°C., Eq. (6.30) may be used to compute ΔF° at 504.9°K., where liquid and solid tin are in equilibrium. Thus $\log K_{504.9} = -1.944$, and since

$$\Delta F^\circ = -RT \ln K, \quad \Delta F^\circ_{504.9} = +4,490 \text{ cal.}$$

The heat of reaction (6.23) is given by Eq. (6.25) with

$$\Delta H_0 = 12,800.$$

Substituting this equation in (6.16) gives

$$\begin{aligned}
 & -d\left(\frac{\Delta F^\circ}{T}\right) \\
 & = \left(\frac{12,800 - 4.06T + 0.765 \times 10^{-3}T^2 - 1.26 \times 10^5T^{-1}}{T^2}\right) dT,
 \end{aligned} \tag{6.31}$$

which when integrated yields

$$\begin{aligned}
 -\Delta F^\circ = & -12,800 - 4.06T \ln T + 0.765 \times 10^{-3}T^2 \\
 & + 0.63 \times 10^5T^{-1} + I'T.
 \end{aligned} \tag{6.32}$$

The integration constant I' may be determined from the value for ΔF° at 504.9°K. Solving in this manner, the following equation is obtained for reaction (6.23):

$$\begin{aligned}
 -\Delta F^\circ = & -12,800 - 9.36T \log T + 0.765 \times 10^{-3}T^2 \\
 & + 0.63 \times 10^5T^{-1} + 41.18T,
 \end{aligned} \tag{6.33}$$

and therefore

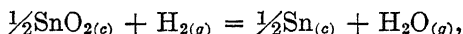
$$\begin{aligned}
 \Delta F^\circ_{298.1} & = 7,150 \text{ cal.} \\
 \Delta S_{298.1} & = \frac{\Delta H - \Delta F^\circ}{T} = \frac{11,250 - 7,150}{298.1} = 13.75 \text{ cal./deg.}
 \end{aligned}$$

The above heat-capacity equations have been taken from the compilation of Kelley, with the exception of the value for $\text{H}_2\text{O}_{(g)}$ which is due to Gordon.³ No attempt has been made to correct the heat of formation of SnO_2 for crystallographic transitions, since these heats of transition are of smaller magnitude than the uncertainty in the B-R value for the heat of formation of SnO_2 . For this same reason and the fact that the heat-capacity equation for SnO_2 is an estimated one, it has been considered advisable to ignore the β to γ transition in tin at 161°C.

6. Calculation of I from the Third Law.—In Sec. 5 it was found that the integration constant I of the equation expressing K as a function of T could be evaluated from a few experimental determinations of K , in conjunction with auxiliary data consisting of one value for the heat of the reaction and the heat capacities of the substances involved. When these same auxiliary data are available, plus the heat capacities of each of the substances involved down to low temperatures ($<90^\circ\text{K.}$), it is possible to make a third-law calculation of the entropies of the various substances in their reference states, and hence compute the ΔS term in the equation

$$\Delta F^\circ = \Delta H - T\Delta S.$$

Thus, for the reaction considered in Sec. 5,



it will be seen by consulting Chap. VIII that the third-law entropies of all these substances are known at 25°C.; hence it is possible to compute $\Delta S_{298.1}$ and compare this value with the value derived from the equilibrium studies of Emmett and Schultz.²

$$\begin{aligned} \Delta S &= S_{\text{H}_2\text{O}} + S_{\frac{1}{2}\text{Sn}} - S_{\text{H}_2} - S_{\frac{1}{2}\text{SnO}_2} & (6.34) \\ \Delta S_{298.1} &= 45.13 + 6.15 - 31.23 - 6.25 = 13.80 \text{ cal./deg.} \end{aligned}$$

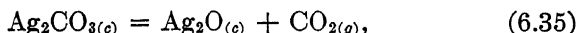
In illustration 2b, it will be noticed that the standard entropy change at 25°C., computed from equilibrium measurements, is 13.75 cal./deg. The excellent agreement between the two entropy changes, arrived at by such widely different types of experimental techniques, is probably fortuitous in this case, owing to uncertainties in the auxiliary data employed in the above illustrative problem. Having obtained $\Delta S_{298.1}$ from the third law and knowing the heat of the reaction, we may readily compute $\Delta F^\circ_{298.1}$; hence the integration constant of the $\Delta F^\circ - T$ or $\ln K - T$ equation may be obtained.

The following problem is designed to illustrate the use of third-law entropies in estimating decomposition temperatures of pure compounds as a matter of laboratory interest.

7. Use of Third Law in Predicting Decomposition Pressures.

Illustration 3.—Moist silver carbonate is to be dried in an oven at 110°C. Should CO_2 be circulated through the oven in order to repress decomposition and, if so, what is the minimum percentage CO_2 to be maintained in the drying air?

Solution.—Assuming that the course of the decomposition is represented by the equation



the decomposition pressure at any temperature may be computed from the equilibrium constant of this reaction. Thus,

$$K = P_{\text{CO}_2} \left(\frac{A_{\text{Ag}_2\text{O}}}{A_{\text{Ag}_2\text{CO}_3}} \right) \quad (6.36)$$

and if no solid solutions are formed, $K = P_{\text{CO}_2}$.

The entropies of these substances are found in Tables 7, 21, and 34, Chap. VIII, and consequently

$$\begin{aligned}\Delta S_{298.1} &= S_{\text{CO}_2} + S_{\text{Ag}_2\text{O}} - S_{\text{Ag}_2\text{CO}_3} \\ \Delta S_{298.1} &= 51.08 + 29.09 - 40.0 = 40.17 \text{ cal./deg.}\end{aligned}\quad (6.37)$$

From B-R the heat of the reaction is

$$\Delta H = -94,036 - 6,950 + 119,900 = 18,910 \text{ cal.}$$

Heat-capacity data at elevated temperatures are not available for Ag_2CO_3 and Ag_2O ; consequently these items are estimated from Kopp's law (Chap. II, Sec. 4) as 26.2 and 16.4 cal./deg., respectively. Using 9.6 as a rough average for the heat capacity of CO_2 gives

$$\Delta C_p = 9.6 + 16.4 - 26.2 \simeq 0;$$

hence the ΔH of the reaction is substantially constant with temperature. Substituting the appropriate values in Eq. (6.17) and integrating give

$$\log P_{\text{CO}_2} = \frac{-18,910}{4.575T} + I = \frac{-4,138}{T} + I. \quad (6.38)$$

The integration constant may readily be determined from the ΔH and ΔS , given above; thus,

$$\begin{aligned}\Delta F^\circ_{298.1} &= 18,910 - 40.17T, \\ -4.575T \log P_{\text{CO}_2} &= 18,910 - 40.17T, \\ \log P_{\text{CO}_2} &= \frac{-4,138}{T} + \frac{40.17}{4.575};\end{aligned}$$

consequently, the integration constant of Eq. (6.38) is

$$\frac{\Delta S_{298.1}}{2.303R} = 8.780.$$

Therefore

$$\log P_{\text{CO}_2} = \frac{-4,138}{T} + 8.780 \quad (6.39)$$

and, at 383.1°K.,

$$\begin{aligned}\log P_{\text{CO}_2} &= \frac{-4,138}{383.1} + 8.780 = -2.022, \\ P_{\text{CO}_2} &= 9.51 \times 10^{-3} \text{ atm.}\end{aligned}$$

In other words, if the drying air contains about 1 to 2 per cent CO_2 by volume, the decomposition of the Ag_2CO_3 should be repressed at 110°C .

8. Calculation of I from Electromotive-force Measurements.—

One of the most convenient and accurate procedures for performing physical and chemical changes of state under reversible, isothermal conditions is by means of electrochemical processes. Since the free-energy decrease suffered by a system in going from the initial to the final state at constant pressure is the non-mechanical work obtainable under reversible, isothermal conditions, it follows that the electrical work produced by the change in state also measures the free-energy decrease. Now, whenever Q coulombs of electricity are transferred from a point of lower potential to a point E volts above it, the electrical work done is by definition, EQ ; hence

$$-\Delta F = EQ. \quad (6.40)$$

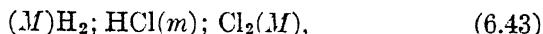
For chemical purposes the unit quantity of electricity is not the single coulomb, but the number of coulombs required to deposit the gram equivalent of a univalent substance, which is called the "faraday" and equals 96,494 coulombs. Thus, if the electrochemical process under consideration involves the passage of N faradays of electricity at a potential of E volts, the free-energy decrease is

$$-\Delta F = 96,494NE \text{ in joules} \quad (6.41)$$

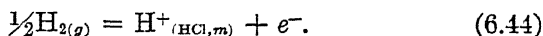
or

$$-\Delta F = 23,066NE \text{ in calories.} \quad (6.42)$$

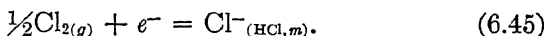
In order to be able to measure the E corresponding to the required change in state, it is necessary for the change of state to take place under conditions yielding electrical energy. This can be done if the process can be treated as an oxidation-reduction reaction, which can be made to take place in a cell consisting of two electrodes, in which the oxidation process occurs at one electrode and the reduction process at the other. Thus, if a cell is visualized as consisting of an inert metal electrode, such as platinum, surrounded by an atmosphere of hydrogen, plus a similar electrode surrounded by an atmosphere of chlorine, with both electrodes dipping in a solution of HCl of definite molality, as represented by the scheme



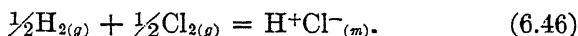
then the processes that occur in such a cell, when the electrodes are connected externally by means of an electrical conductor, are
Oxidation:



Reduction:



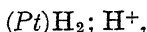
Consequently the over-all change in state for the cell as a whole corresponds to the process



If electricity were permitted to flow through this cell, and if this cell contained a large enough quantity of hydrochloric acid—such that the formation of additional HCl made little difference in the acid concentration—and the electromotive force were measured from time to time, it would be found that the potential constantly decreased and the rate of formation of HCl declined. Closer examination of conditions within the cell would disclose sensible concentration and temperature gradients; hence, such a process is not the reversible process required to evaluate free-energy changes. Fortunately, it is not necessary to measure the electrical energy produced by the actual formation of a whole mole of HCl; but if the electromotive force developed by the formation of an infinitesimal quantity of HCl be measured by a potentiometer, such a process is reversible when the two are in balance. It is only necessary to multiply this reversible electromotive force by the quantity of electricity that would have to flow in order to produce a mole to determine $-\Delta F$. If the H_2 and Cl_2 are at 1 atm. pressure, the measured electromotive force may readily be adjusted to the value for these substances in their standard reference state of unit fugacity. If the activity coefficient of the HCl at the molality m is known, it is then possible to compute the standard free energy of formation of HCl in solution at unit activity.

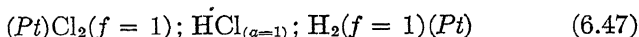
In dealing with electrochemical problems, it is well to bear in mind the following accepted conventions regarding cells and their electromotive forces:

a. In the absence of a wholly acceptable, unambiguous method for determining potentials on an absolute scale, the potential of the electrode,



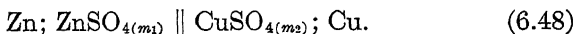
at all temperatures is taken as zero, when the H_2 is present at unit fugacity and the mean ion activity of the hydrogen ion in solution equals unity. In the absence of notation to the contrary, all gases are to be considered at unit fugacity.

b. The single electrode potential of any other half cell is equal to the electromotive force of the whole cell, formed by combining it with the standard hydrogen electrode defined in *a*—all concentrations corresponding to unit activity for solutions and unit fugacities for gases. Thus, in the case of the chlorine electrode employed in the above cell, the standard single electrode potential of the chlorine electrode represents the electromotive force of the whole cell:

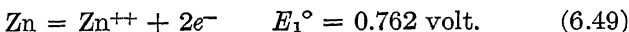


for which $E^\circ = -1.358$ volts at $25^\circ C$.

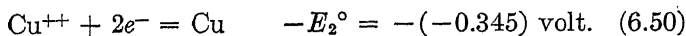
c. All couples are written with the reduced form on the left-hand side of the half-cell equation and electrons on the right-hand side. The oxidizing electrode, or the one at which electrons are given off, is placed on the left side of the cell representation; and the reducing electrode, or the electrode at which electrons are absorbed, is placed on the right. If the sum of the half-cell potentials is positive when arranged in this manner, the cell reaction can take place spontaneously and the system experiences a decrease in free energy. If the sum is negative, the process cannot take place in the direction indicated without the application of an external electromotive force and the expenditure of electrical energy from an external source. Thus, according to these conventions, the following processes occur in the cell:



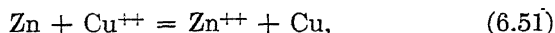
Left: Oxidation:



Right: Reduction:



Adding these two half-cell equations gives

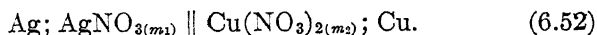


for the over-all change of state. The net electromotive force of the cell is

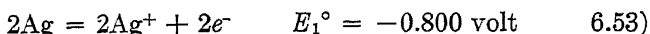
$$E^\circ = E_1^\circ + (-E_2^\circ) = 0.762 + 0.345 = 1.107 \text{ volts},$$

and the reaction will go in the direction written. It will be noticed that, in performing the addition, the sign of E_2° has been reversed. This is because the sign of all recorded half-cell potentials corresponds to the half-cell reaction written with the reduced form on the left side and the electrons on the right; since the half-cell process was written in the opposite direction, the opposite sign must be used.

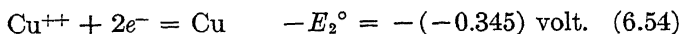
Again, consider the cell,



Left: Oxidation:



Right: Reduction:



By addition, the over-all change of state is



and the over-all electromotive force is

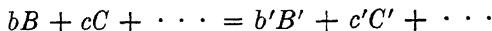
$$E^\circ = E_1^\circ + (-E_2^\circ) = -0.455 \text{ volt}.$$

Thus, this cell cannot function spontaneously in the direction indicated and silver cannot reduce cupric ion. In general, the reduced form of any couple that is more positive than a second couple is capable of reducing the oxidized form of the second couple.

It will be noticed that the two cells represented by (6.48) and (6.52) contain two different electrolytes separated by a double bar. This symbol is used to indicate the existence of a liquid-liquid potential at the junction of the two electrolytes, which has been deducted from electromotive force of the cell. That is, the over-all electromotive forces given for these cells represent just

the sum of the electromotive forces for the two half cells, the actual measured values being somewhat greater or less than this value by the magnitude of the liquid-liquid potential.

d. The calculation of electromotive forces of single couples or complete cells may be performed when the fugacities and activities of all the substances involved in the cell process are known. It has been found that the free-energy change accompanying the reaction



is given by the equation

$$\Delta F - \Delta F^\circ = RT \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots} \quad (6.13)$$

Substituting $-\Delta F = NFE$ [Eq. (6.41)] in (6.13) gives the desired equation for computing electromotive forces of voltaic cells,

$$-NFE + NFE^\circ = RT \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots}$$

or

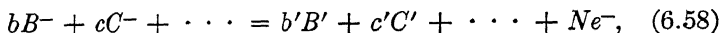
$$E = E^\circ - \frac{RT}{NF} \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots} \quad (6.56)$$

The significance of E° becomes clear when unity is substituted for each activity in the logarithmic term. The electromotive force of the cell is then

$$E = E^\circ \quad (6.57)$$

In other words, E° is the electromotive force of the cell when the activity of each substance involved equals unity; that is, each substance is in its reference state.

In a similar manner it may be shown that the electromotive force corresponding to the half-cell reaction,



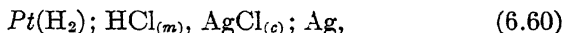
is given by the equation

$$E = E^\circ - \frac{RT}{NF} \ln \frac{a_{B'}^{b'} \cdot a_{C'}^{c'} \cdots}{a_B^b \cdot a_C^c \cdots}, \quad (6.59)$$

where the left-hand side of the equation contains substances in the reduced state. At 25°C. the coefficient of the logarithmic term becomes equal to 0.05914, when E is in volts and the log term refers to the base 10.

e. In some cases, it is not possible to devise a cell capable of producing the desired change of state, owing to unavoidable side reactions, irreversibility of electrodes, etc. However, if the corresponding ΔF° can be evaluated by any of the other standard methods and if the reaction can be resolved into two half-cell reactions, one of which has a known E° , then obviously the true E° value for the unmeasurable half-cell reaction can be computed.

9. Evaluation of ΔF° and ΔS° of Formation from Electromotive-force Measurements. *Illustration 4.*—The cell,



has been the subject of a number of careful researches, and the heat capacities of $\text{AgCl}_{(c)}$ and $\text{Ag}_{(c)}$ have been measured down to low enough temperatures to permit evaluation of the entropy of these substances at 298.1°K. Calculate

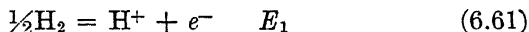
a. The standard electrode potential of this cell from the observation that the electromotive force of the cell equals +0.4586 volt at 25°C., when the HCl molality equals 0.0112, and the fugacity of the H_2 equals unity;

b. The standard free energy of formation of HCl in aqueous solution at unit activity;

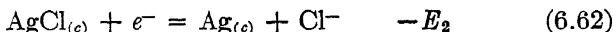
c. The standard entropy of formation of HCl in aqueous solution at unit activity and the entropy of the chloride ion.

Solution.—a. The change of state for the cell represented by (6.60) is the sum of the two half-cell processes:

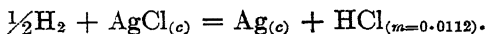
Oxidation:



Reduction:



Over-all change of state:



Total electromotive force:

$$E = E_1 + (-E_2) = E_1^\circ - E_2^\circ - \frac{RT}{F} \ln \frac{a_{\text{HCl}}}{f_{\text{H}_2}^{1/2}}.$$

Therefore

$$E_2^\circ = -E - \frac{RT}{F} \ln (\gamma m)^2_{\text{HCl}}, \quad (6.63)$$

since the observed E corresponds to $f_{\text{H}_2} = 1$, and by convention $E_1^\circ = 0$.

Referring to Fig. 19, Appendix 4, the activity coefficient of HCl at $m = 0.0112$ is 0.903; therefore

$$\begin{aligned} E_2^\circ &= -0.4586 - 2(0.05914) \log (0.903)(0.0112) \\ &= -0.4586 - 0.1183 \log 1.0114 \times 10^{-2} = -0.2220 \text{ volt.} \end{aligned}$$

b. The standard electromotive force of cell (6.60) is

$$E^\circ = E_1^\circ + (-E_2^\circ) = 0 + 0.2220,$$

consequently the standard free-energy change for this process is

$$-\Delta F^\circ_{298.1} = NFE = 23,066(0.2220) = 5,121 \text{ cal.}$$

In order to evaluate the free energy of formation of HCl in its standard state, the free energy of formation of $\text{AgCl}_{(c)}$ must be evaluated from the third law. In Tables 6, 15, and 33 of Chap. VIII, are found the appropriate entropies to substitute in the equation for the entropy of formation of AgCl:

$$\begin{aligned} \Delta S_{298.1} &= S_{\text{AgCl}} - S_{\text{Ag}} - S_{\frac{1}{2}\text{Cl}_2} = 22.97 - 10.2 - 26.66 \\ &= -13.89. \quad (6.64) \end{aligned}$$

The heat of formation of $\text{AgCl}_{(c)}$ is given in B-R as $-30,300$ cal.; hence

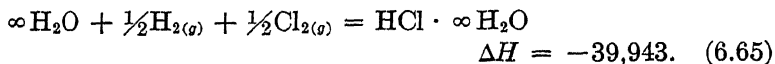
$$\Delta F^\circ_{298.1} = -30,300 + 298.1(13.89) = -26,160 \text{ cal./mole.}$$

Combining this value with the standard free-energy change for cell (6.60) gives

$$\Delta F^\circ_{298.1} = -31,280 \text{ cal.}$$

for the formation of 1 mole of HCl in aqueous solution at unit activity.

c. The standard entropy of formation of HCl at unit activity may be evaluated from the known heat of formation in the standard reference state. The standard state for electrolytes in water is the hypothetical state of unit activity with the heat content equal to its value at infinite dilution. From Chap. III, Sec. 2, this value is $-39,943$ cal./mole, corresponding to the process,



Combining this value with the above value for ΔF° gives

$$\Delta S^\circ_{298.1} = \frac{\Delta H - \Delta F^\circ}{T} = \frac{-39,943 + 31,280}{298.1} = -29.06.$$

Since electromotive-force calculations are based on the conventions that the free-energy and heat content of the hydrogen ion at unit activity and all temperatures equals zero, it also follows that the entropy of the H^+ under these conditions equals zero and, therefore, this ΔS° of formation equals the ΔS° of formation of Cl^- at unit activity. The entropy of Cl^- under these conditions is therefore

$$\Delta S^\circ = -29.06 = S^\circ_{Cl^-} - S^\circ_{\frac{1}{2}H_2} - S^\circ_{\frac{1}{2}Cl_2}. \quad (6.66)$$

Therefore

$$S^\circ_{Cl^-} = -29.06 + 42.27 = +13.21 \text{ cal./}(\text{mole})(\text{deg}).$$

10. Computation of ΔF° from Known Free Energies of Formation of Substances Involved.—A constantly increasing list of compounds of known free energies of formation at $25^\circ C.$ is being developed. These values have been determined by one or more of the three fundamental methods just described, namely, equilibrium measurements, the third law, or electromotive-force measurements. Eventually, the free energies of formation of all known compounds will be available, and it will be possible to compute the standard free-energy change of any reaction at $25^\circ C.$ by simple addition and subtraction of free energies of formation.

It should be remembered, however, that this is only a small part of the data required for the successful study of the equilibrium of physical and chemical processes. Equally important data on enthalpy changes and heat capacities are required in order to evolve a useful picture of the behavior of the system under varying conditions of temperature, pressure, and concentrations.

11. Evaluation of Enthalpy and Entropy Changes from Electromotive-force Data.—If the relation $-\Delta F^\circ = NFE^\circ$ is substituted in Eq. (5.11), the following equation is obtained:

$$\left[\frac{\partial(-NFE^\circ)}{\partial T} \right]_P = \frac{-NFE^\circ - \Delta H}{T}, \quad (6.67)$$

or

$$\Delta H = NFT \left[\left(\frac{\partial E^\circ}{\partial T} \right)_P - \frac{E^\circ}{T} \right], \quad (6.68)$$

or

$$\Delta H = -NFE^\circ + NFT \left(\frac{\partial E^\circ}{\partial T} \right)_P. \quad (6.69)$$

Since

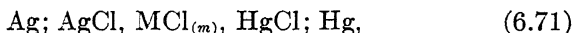
$$\Delta H = \Delta F^\circ + T\Delta S^\circ,$$

it follows that

$$\Delta S^\circ = NF \left(\frac{\partial E^\circ}{\partial T} \right)_P. \quad (6.70)$$

Thus, when the temperature coefficient of the standard electromotive force of a cell has been determined experimentally, it is possible to compute the enthalpy and entropy changes corresponding to the change of state occurring in the cell by means of Eqs. (6.69) and (6.70).

Illustration 5.—The electromotive force and temperature coefficient of the cell:



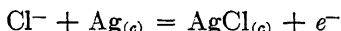
have been measured by Gerke.⁴ From the fact that $E^\circ = 0.0455$ volt and $(dE^\circ/dT) = 3.38 \times 10^{-4}$ volt/deg. at 25°C ., evaluate:

a. the change of state occurring in this cell when 1 faraday of electricity passes through the cell;

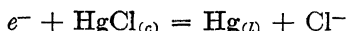
b. the standard free-energy, enthalpy, and entropy changes corresponding to the cell process;

c. the free energy and heat of formation of $\text{HgCl}_{(c)}$ and the entropy of $\text{HgCl}_{(c)}$. Use necessary auxiliary data from illustration 4. The entropy of liquid Hg at 25°C . equals 18.5 cal./(deg.) (g. atom).

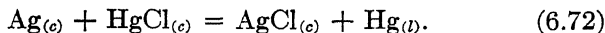
Solution.—a. The cell process is the sum of
Oxidation:



and reduction:



Over-all:



$$b. \quad -\Delta F^\circ_{298.1} = (23,066)(0.0455) = 1,050 \text{ cal.}$$

From Eq. (6.68)

$$\Delta H = (23,066)(298.1) \left(3.38 \times 10^{-4} - \frac{4.55 \times 10^{-2}}{298.1} \right),$$

$$\Delta H_{298.1} = (23,066)(298.1)(1.854)10^{-4} = 1,275 \text{ cal.}$$

From Eq. (6.70)

$$\Delta S^\circ = (23,066)(3.38)10^{-4} = 7.796 \text{ cal./degree.}$$

c. To compute the free energy and heat of formation of $\text{HgCl}_{(c)}$:

For reaction (6.72):

$$\begin{aligned}\Delta F^\circ_{298.1} &= -1,050 = \Delta F^\circ_{\text{AgCl}} - \Delta F^\circ_{\text{HgCl}} \\ \Delta H_{298.1} &= 1,275 = \Delta H_{\text{AgCl}} - \Delta H_{\text{HgCl}}.\end{aligned}$$

From illustration 4:

$$\Delta F^\circ_{\text{AgCl}} = -26,160, \quad \Delta H_{\text{AgCl}} = -30,300.$$

Therefore

$$\Delta F^\circ_{\text{HgCl}} = -26,160 + 1,050 = -25,110 \text{ cal./mole.}$$

Therefore

$$\Delta H_{\text{HgCl}} = -30,300 - 1,275 = -31,575 \text{ cal./mole.}$$

Since the entropy of $\text{AgCl}_{(c)} = 22.97$ units at 25°C. and

$$\begin{aligned}\Delta S^\circ &= 7.80 = S_{\text{AgCl}} + S_{\text{Hg}} - S_{\text{HgCl}} - S_{\text{Ag}}, \\ S_{\text{HgCl}} &= 22.97 + 18.5 - 10.2 - 7.80 = 23.47 \text{ cal./mole(deg.).}\end{aligned}$$

12. Evaluation of Heats of Reaction from Equilibrium Measurements.—It is possible to obtain reliable values for heats of reaction and heats of formation from a series of measured equilibrium constants when the necessary heat capacities are available. Referring to Eq. (6.21) for $\ln K$ vs. T , it will be noted that the quantity Σ , which is equal to $I - \frac{\Delta H_0}{T}$, is directly computable from the experimental quantity,

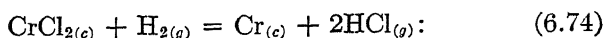
$$\Sigma = R \ln K - \Delta a \ln T - \frac{\Delta b}{2} T + \frac{\Delta c}{2} T^{-2}. \quad (6.73)$$

Consequently, if calculated values for Σ are plotted vs. $1/T$, the slope of this straight-line plot gives ΔH_0 directly, and the heat of the reaction may be computed at any other temperature from the relation

$$\Delta H = \Delta H_0 + \Delta aT + \frac{\Delta b}{2} T^2 + \Delta cT^{-1}.$$

By this method it is very often possible to supplement indirect calorimetric data of questionable accuracy with more reliable values.

Illustration 6.—The ΔH of formation of $\text{CrCl}_{2(c)}$ recorded in B-R is $-103,100$. Since this datum was obtained indirectly from heats of solution measurements, an independent determination of the heat of formation would be desirable. Doerner⁵ obtained the following equilibrium constants for the reaction



| Temperature, °C. | $K_{\text{av.}}$ |
|------------------|------------------------|
| 632 | 1.976×10^{-5} |
| 677 | 6.614×10^{-5} |
| 725 | 2.104×10^{-4} |
| 772 | 5.533×10^{-4} |
| 806 | 1.120×10^{-3} |

where $K = P_{\text{HCl}}^2/P_{\text{H}_2}$ and the pressures are in atmospheres.

a. Derive an expression for the ΔH of this reaction as a function of temperature.

b. Compute the heat of formation of $\text{CrCl}_{2(c)}$ at 18°C . The heat of formation of $\text{HCl}_{(g)}$ is $-22,060$ cal./mole at 18°C .

Solution.—*a.* The constants of the Σ function may be evaluated from the constants of the equation for ΔC_p .

For reaction (6.74):

$$\begin{aligned} 2\text{HCl}_{(g)} C_p &= 13.40 + 1.68 \times 10^{-3}T \\ \text{Cr}_{(c)} C_p &= 4.84 + 2.95 \times 10^{-3}T \\ \text{Sum} &= 18.24 + 4.63 \times 10^{-3}T \\ \text{CrCl}_{2(c)} C_p &= 15.23 + 5.30 \times 10^{-3}T \\ \text{H}_{2(g)} C_p &= 6.62 + 0.81 \times 10^{-3}T \\ \text{Sum} &= 21.85 + 6.11 \times 10^{-3}T \end{aligned}$$

Therefore

$$\Delta C_p = -3.61 - 1.48 \times 10^{-3}T. \quad (6.75)$$

The constants to be substituted in the Σ Eq. (6.73) are

$$\Delta a = -3.61 \quad \Delta b = -1.48 \times 10^{-3} \quad \Delta c = 0.$$

Therefore

$$\Sigma = 4.575 \log K + 3.61(2.303) \log T + 0.74 \times 10^{-3}T. \quad (6.76)$$

Substituting the above values for K and T in this equation gives the following values for Σ :

| Temperature, °K. | log T | K | $-4.575 \log K$ | Σ |
|---------------------|---------|------------------------|-----------------|----------|
| 905 | 2.95665 | 1.976×10^{-5} | 21.521 | 3.729 |
| 950 | 2.97772 | 6.614×10^{-5} | 19.121 | 6.340 |
| 998 | 2.99913 | 2.104×10^{-4} | 16.822 | 8.852 |
| 1045 | 3.01912 | 5.533×10^{-4} | 14.901 | 10.973 |
| 1079 | 3.03302 | 1.120×10^{-3} | 13.500 | 12.513 |

These values of Σ are plotted versus $1/T$ on Fig. 7. The estimated slope of the graph corresponds to a ΔH_0 of 49,300 cal. The required equation for the heat of this reaction is, therefore

$$\Delta H = 49,300 - 3.61T - 0.74 \times 10^{-3}T^2. \quad (6.77)$$

b. The heat of the reaction at 18°C. is then

$$\begin{aligned} \Delta H_{291.1} &= 49,300 \\ &- 3.61(291.1) - (7.4)(2.91)^2 \\ &= 48,190 \text{ cal.} \end{aligned}$$

Consequently

$$48,190 = \Delta H_{2\text{HCl}} - \Delta H_{\text{CrCl}_2}.$$

Therefore

$$\begin{aligned} \Delta H_{\text{CrCl}_2} &= -44,120 - 48,190 \\ &= -92,310 \text{ cal./mole.} \end{aligned}$$

The above data may also be employed to evaluate I , and hence the equation for the standard free-energy change of this reaction. The usual procedure is to compute I for each value of K employing the average value of ΔH_0 estimated from the $\Sigma - 1/T$ plot. These values of I are then averaged and the average value is used to complete the equation for ΔF° or $\ln K$ as a function of T . By this method Doerner obtained 38,528 cal. for ΔF° at 25°C. for reaction (6.74), corre-

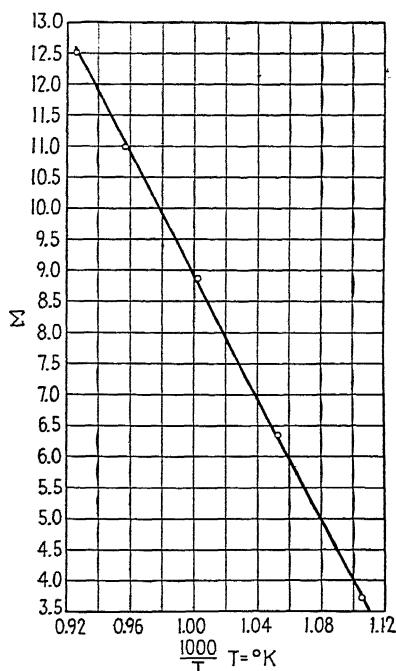
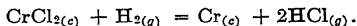


FIG. 7.— Σ plot for evaluating ΔH_0 of reaction:



sponding to a free energy of formation of $\text{CrCl}_{2(c)}$ of $-84,080$ cal./mole.

13. Effect of Pressure on the Equilibrium Constant.—Since the ΔF° of a reaction represents the difference between the sums of the molar free energies of the products and reactants entering a given reaction in their chosen reference states, and since these quantities depend only on the temperature, it follows that the equilibrium constant for the reaction defined by the equation

$$K = e^{-\Delta F^\circ/RT} \quad (6.78)$$

depends only on the temperature and is independent of the pressure. However, in the derivation of this equation the actual molar free energy of each constituent present in the system was expressed by means of an equation of the form

$$F_i - F_i^\circ = RT \ln a_i; \quad (6.79)$$

consequently it is important that the stoichiometric units employed to evaluate K are true measures of the difference between the molar free energies in the reference states and in the actual equilibrium system. When dealing with gaseous systems at pressures less than 3 or 4 atm., the partial pressures of the individual components of the system may be used as this measure; hence

$$F_i - F_i^\circ = RT \ln P_i = RT \ln N_i P, \quad (6.80)$$

where P represents the total pressure on the system. At higher pressures, fugacities or the true thermodynamic measure of the escaping tendency must be employed. When this is done, the expression for the equilibrium constant (6.14) becomes

$$K = \frac{f_{B'} \cdot f_{C'} \cdot \cdot \cdot}{f_{B''} \cdot f_{C''} \cdot \cdot \cdot} \quad (6.81)$$

As pointed out in Chap. V, Sec. 4, it is customary to assume that, in a mixture of gases, the fugacity of each component in the mixture is

$$f_i = f_i^\circ N_i, \quad (6.82)$$

where f_i° represents the fugacity of the pure i th component at the total pressure P on the system. Substituting these values in Eq. (6.81) gives:

$$K = \frac{(f_{B'}^\circ)^{b'}(f_{C'}^\circ)^{c'} \cdots N_{B'}^{b'} \cdot N_{C'}^{c'} \cdots}{(f_B^\circ)^b(f_C^\circ)^c \cdots N_B^b \cdot N_C^c \cdots} \quad (6.83)$$

Or substituting $f_i^\circ = \gamma_i^\circ P$, since

$$\gamma_i^\circ = \frac{f_i}{P_i} = \frac{f_i^\circ}{P},$$

by assumption, yields

$$K = \left[\frac{(\gamma_{B'}^\circ)^{b'}(\gamma_{C'}^\circ)^{c'} \cdots N_{B'}^{b'} \cdot N_{C'}^{c'} \cdots}{(\gamma_B^\circ)^b(\gamma_C^\circ)^c \cdots N_B^b \cdot N_C^c \cdots} \right] P^{b'+c'+\cdots-(b+c+\cdots)} \quad (6.84)$$

Equation (6.84) is adaptable to practical applications, since estimated activity coefficients may readily be obtained from the universal charts of activity coefficients as a function of reduced pressures and temperatures.

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CHAPTER VII

SPECIAL METHODS (THEORETICAL)

Technical problems frequently arise, in which it is necessary to estimate or guess at thermochemical data required to evaluate a preliminary answer to them. Since these problems are usually concerned with gross heat effects accompanying a certain process or equilibrium conditions and their dependence on temperature, the data to be estimated may consist of one or more of the following items: (a) heat capacities; (b) enthalpy changes accompanying changes of state or crystallographic transitions; (c) enthalpy changes accompanying chemical reactions; (d) entropies and entropy changes; (e) free-energy changes. Fundamentally, item (e) need not be regarded as a separate entity, since free-energy changes may be computed from the other four items when available; consequently the direct estimation of free energies is of more theoretical than practical importance. Some generalizations have been given for estimating enthalpy changes accompanying fusion and vaporization processes (Chap. III), but unfortunately, as pointed out in Chap. IV, no theoretically sound methods are available for estimating enthalpy changes in chemical reactions. Consequently, it will be found that most of the theoretical or semiempirical methods available for computing thermochemical data are concerned chiefly with the heat capacities and entropies of solids and gases. For convenience the subject matter of Chaps. VII and VIII has been divided into theoretical and semiempirical methods.

1. Partition Functions.—From theoretical considerations, in conjunction with the experimental data obtained from spectroscopy and the measurement of heat capacities of gases, it is known that molecules in the gaseous state possess internal energy, in addition to the external energy associated with the three translational degrees of freedom of the molecule. This internal energy is distributed over degrees of freedom which are associated with the mutual vibrations of its constituent nuclei (vibrational degrees of freedom), with the rotation of the molecule as a whole

(rotational degrees of freedom), and with changes of configuration of its constituent electrons. In addition there are numerous cases involving single bonds connecting groups of atoms, about which rotational motion of these groups is possible. These internal degrees of freedom differ from the translational degrees of freedom in that the energy associated with any given degree of freedom cannot assume a continuous series of values but is restricted to a series of discrete values called "energy levels" or "stationary states." For this reason it is customary to treat the internal energy of a gas separately from its translational energy, and, accordingly, the internal energy of a molecule may be expressed by the equation

$$\epsilon_i = \epsilon_{\text{rot.}} + \epsilon_{\text{i.rot.}} + \epsilon_{\text{vib.}} + \epsilon_{\text{el.}} \quad (7.1)$$

Obviously, if equations can be developed for computing the number of molecules per mole occupying each energy level at any temperature, and if some experimental procedure is available for determining the energy of each level above the lowest vibrational and rotational state of the lowest electronic level, these energies, when multiplied by the number in each level and summed over all possible levels, will give the internal energy per mole of the gas referred to the absolute zero, *i.e.*, the energy in excess of the zero-point energy. And since, by definition, the heat capacity at constant volume is the derivative of E with respect to T , the "internal" heat capacity may be calculated at any temperature. Furthermore, the entropy of the gas by the third law is $\int_0^T C d \ln T$; consequently, after C has been computed, the entropy associated with the internal degrees of freedom may be evaluated. In a similar manner the other thermodynamic functions of interest are derived. It is then necessary to add only the contribution from translational degrees of freedom in order to obtain the usual thermodynamic functions to be employed in practical thermochemical considerations.

It will be shown, actually, in Sec. 2, that all the required thermodynamic functions may be computed by performing various algebraic operations on one single quantity, which is a characteristic of the gas under consideration at any temperature. This quantity is called the "partition function" or "state sum" and is defined by the equation

$$Q = p_0 e^{-0/kT} + p_1 e^{-\epsilon_1/kT} + p_2 e^{-\epsilon_2/kT} + \dots = \sum p_i e^{-\epsilon_i/kT}. \quad (7.2)$$

In this equation ϵ_i represents the energy of any level above the ground level, k the Boltzmann constant (R divided by the Avogadro number), and p_i represents the number of levels, possessing energy differing by such small amounts from the value ϵ_i , that, for all practical purposes, these groups of levels may be treated as p_i levels of identical energy, ϵ_i . The p 's are called "statistical weights," "quantum weights," or, sometimes, the "degeneracy of the level." The appropriate numerical values to be substituted for the energy levels are obtained from the experimental data of spectroscopy, and the statistical weights are furnished by the theoretical results of the quantum mechanics. The derivation of the Boltzmann factor, $e^{-\epsilon_i/kT}$, is given in Tolman, "Statistical Mechanics."¹

2. General Treatment.—The following is an outline of the method for computing thermodynamic functions of perfect gases from partition functions, as given by Giauque² in 1930. The energy levels and partition functions considered are those corresponding to internal degrees of freedom. If A represents the number of molecules per mole in the lowest internal energy state or ground level; then, according to the Maxwell-Boltzmann distribution law, the number of molecules in any state possessing the energy ϵ_i above the ground level at the absolute temperature T is

$$N_i = A p_i e^{-\epsilon_i/kT}. \quad (7.3)$$

Since N molecules are distributed over all possible energy levels,

$$N = A p_0 + A p_1 e^{-\epsilon_1/kT} + A p_2 e^{-\epsilon_2/kT} + \dots = A \sum p_i e^{-\epsilon_i/kT} = A Q. \quad (7.4)$$

According to Eq. (7.4), the partition function for the internal degrees of freedom represents the reciprocal of the mole fraction of the molecules occupying the ground level. From Eq. (7.3), the i th energy level contributes $\epsilon_i A p_i e^{-\epsilon_i/kT}$ ergs of energy to the molar internal energy; hence the total internal energy at the temperature T is

$$E_{\text{int.}}^\circ = E_0^\circ + o p_0 A + \epsilon_1 A p_1 e^{-\epsilon_1/kT} + \epsilon_2 A p_2 e^{-\epsilon_2/kT} + \dots, \quad (7.5)$$

where E_0° represents the energy at the absolute zero (the zero-point energy) and the zero superscript indicates the ideal gas

state at 1 atm., since the internal energy levels contributing to (7.5) are not influenced by intermolecular forces. Thus the internal energy in excess of the zero-point energy is

$$E_{\text{int}}^{\circ} - E_0^{\circ} = A \sum \epsilon_i p_i e^{-\epsilon_i/kT}.$$

Substituting A from (7.4) gives

$$E_{\text{int}}^{\circ} - E_0^{\circ} = \frac{N \sum \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum p_i e^{-\epsilon_i/kT}} = RT^2 \frac{d \ln Q}{dT} = -R \frac{d \ln Q}{d(1/T)}. \quad (7.6)$$

Hence the internal heat capacity at constant volume is

$$C_v = \frac{dE_{\text{int}}^{\circ}}{dT} = \frac{N}{kT^2} \left[\frac{\sum \epsilon_i^2 p_i e^{-\epsilon_i/kT}}{\sum p_i e^{-\epsilon_i/kT}} - \left(\frac{\sum \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum p_i e^{-\epsilon_i/kT}} \right)^2 \right] \quad (7.7)$$

or, substituting from (7.6),

$$C_v = -R \frac{d}{dT} \left[\frac{d \ln Q}{d(1/T)} \right] = \frac{R}{T^2} \frac{d^2 \ln Q}{d(1/T)^2}. \quad (7.8)$$

The entropy associated with the internal degrees of freedom is, therefore,

$$dS = \frac{dE^{\circ}}{dT} d \ln T. \quad (7.9)$$

Substituting (7.8) gives

$$S^{\circ} - S_0^{\circ} = -R \int_0^T \frac{d}{dT} \left[\frac{d \ln Q}{d(1/T)} \right] d \ln T. \quad (7.10)$$

Therefore

$$S^{\circ} - S_0^{\circ} = R \left(\ln Q - \ln Q_0 + T \frac{d \ln Q}{dT} \right). \quad (7.11)$$

In this equation Q_0 represents the value of the partition function at the absolute zero, which is simply p_0 —the number of levels having substantially the same energy as the ground level. Since entropy is proportional to the logarithm of the number of states or configurations in which a system of fixed energy may exist, it follows that

$$S_0^{\circ} = R \ln Q_0 = R \ln p_0, \quad (7.12)$$

and, therefore, the internal entropy at the temperature T is

$$S^{\circ} = R \left(\ln Q + T \frac{d \ln Q}{dT} \right). \quad (7.13)$$

It should be noted that, although Eqs. (7.8) and (7.13) represent compact analytical equations for C and S , they are actually employed in the form of summation equations, such as (7.7), for actual numerical calculations. Thus the Q sum must be computed by substituting the appropriate p , ϵ , and T values in (7.2), and $\frac{d \ln Q}{dT}$ may be computed from these same values using the summation equation

$$\frac{d \ln Q}{dT} = \frac{1}{kT^2} \frac{\sum \epsilon p e^{-\epsilon/kT}}{Q}. \quad (7.14)$$

Furthermore, although the values of p and ϵ are independent of temperature, the contribution of a given energy level to the various sums is sharply dependent on temperature because of the exponential factor. When the ratio of ϵ to kT is seven or greater, the exponential factor is less than 0.00091; hence the contribution of this level to the various sums may be neglected.

The total entropy may now be evaluated by adding the contribution from the three translational degrees of freedom to Eq. (7.13), using the well-known Sackur-Tetrode equation for the entropy of translation of a perfect gas:

$$S^\circ_{tr} = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P + \frac{5}{2}R + C + R \ln R, \quad (7.15)$$

where C is a universal constant, M is the molecular weight of the gas, and P is in atmospheres. Substituting

$$C + R \ln R = -7.267$$

gives

$$S^\circ_{tr} = \frac{3}{2}R \ln M + \frac{5}{2}R \ln T - R \ln P + \frac{5}{2}R - 7.267. \quad (7.16)$$

At the customary reference state of 1 atm. pressure and 298.1°K., this becomes

$$S^\circ_{tr} = 6.863 \log M + 26.00. \quad (7.17)$$

The free energy of 1 mole of a perfect gas in excess of its zero-point energy may now be computed as follows:

By definition

$$F^\circ = H^\circ - TS^\circ_{tr} = E^\circ + PV - TS^\circ_{tr}. \quad (7.18)$$

Now, the energy content of 1 mole of a perfect gas may be expressed as the sum of the zero-point energy, plus the energy of internal degrees of freedom [Eq. (7.6)] and the translational energy. This latter item is equal to $\frac{3}{2}RT$ by the principle of equipartition of energy, and PV is equal to RT for a perfect gas; hence Eq. (7.18) becomes

$$F^\circ = E_0^\circ + RT^2 \frac{d \ln Q}{dT} + \frac{3}{2}RT + RT - TS_T^\circ, \quad (7.19)$$

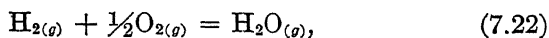
where $RT^2 \frac{d \ln Q}{dT}$ is the internal energy associated with the internal degrees of freedom alone. Substituting Eq. (7.13) plus (7.16) for S_T° finally yields

$$F^\circ - E_0^\circ = RT \ln P - \frac{3}{2}RT \ln M - \frac{5}{2}RT \ln T - RT \ln Q + 7.267T. \quad (7.20)$$

Examination of Eq. (7.20) shows that the computation of the molar free energy in excess of the zero-point energy is considerably easier than the computation of either heat capacities or entropies, since only the comparatively simple Q sum need be evaluated. This is fortunate in view of the fact that the equilibrium constant is of more interest than either of these two functions. Thus, if Eq. (7.20) is divided through by T , a quantity is obtained that directly measures the contribution of each substance to the equilibrium constant of the reaction in question.

$$\frac{F^\circ - E_0^\circ}{T} = R \ln P - \frac{3}{2}R \ln M - \frac{5}{2}R \ln T - R \ln Q + 7.267. \quad (7.21)$$

3. Use of Tables of $(F^\circ - E_0^\circ)/T$.—Data obtained from the analyses of the band spectra of molecules have supplied the necessary values for the energy levels of a good many molecules and have been employed to compute the various thermodynamic functions of these molecules via Eq. (7.2), (7.8), (7.13), and (7.21). Since Eq. (7.21) is particularly important in thermochemical calculations, the method of handling tabulated values of the function $(F^\circ - E_0^\circ)/T$ will be considered in some detail. The standard free-energy change for the reaction,



is equal to

$$\Delta F^\circ = F^\circ_{\text{H}_2\text{O}} - \frac{1}{2}F^\circ_{\text{O}_2} - F^\circ_{\text{H}_2}. \quad (7.23)$$

If the equation $\Delta E_0^\circ = E^\circ_{0(\text{H}_2\text{O})} - \frac{1}{2}E^\circ_{0(\text{O}_2)} - E^\circ_{0(\text{H}_2)}$ is subtracted from Eq. (7.23), the equation

$$\Delta F^\circ - \Delta E_0^\circ = (F^\circ - E_0^\circ)_{\text{H}_2\text{O}} - \frac{1}{2}(F^\circ - E_0^\circ)_{\text{O}_2} - (F^\circ - E_0^\circ)_{\text{H}_2} \quad (7.24)$$

is obtained. Substituting $\Delta F^\circ = -RT \ln K$ in (7.24) gives

$$-R \ln K = \frac{\Delta E_0^\circ}{T} + \left(\frac{F^\circ - E_0^\circ}{T} \right)_{\text{H}_2\text{O}} - \frac{1}{2} \left(\frac{F^\circ - E_0^\circ}{T} \right)_{\text{O}_2} - \left(\frac{F^\circ - E_0^\circ}{T} \right)_{\text{H}_2}. \quad (7.25)$$

Thus, since partition functions have been computed for the H_2O , H_2 , and O_2 molecules from energy levels deduced from the band spectra of these molecules, values for the $(F^\circ - E_0^\circ)/T$ functions are then computed from Eq. (7.21), in the desired range of temperatures, and substituted in Eq. (7.25). However, it will be noticed that the constant ΔE_0° representing the change in the zero-point energy for reaction (7.22) must still be evaluated in order to compute numerical values of K . There are three methods available for evaluating ΔE_0° , of which the first is by far the most widely used.

a. The standard heat of the reaction is determined calorimetrically, and ΔE_0° is then computed from the relations

$$H^\circ = E^\circ + RT$$

$$E^\circ = E_0^\circ + \frac{3}{2}RT + RT^2 \frac{d \ln Q}{dT},$$

and, therefore,

$$\Delta E_0^\circ = \Delta H^\circ - \Delta \left(RT^2 \frac{d \ln Q}{dT} + \frac{5}{2} RT \right). \quad (7.26)$$

b. ΔE_0° may be computed from the relation

$$\Delta F^\circ = -RT \ln K = \Delta(F^\circ - E_0^\circ) + \Delta E_0^\circ \quad (7.27)$$

when both K and the $\Delta(F^\circ - E_0^\circ)$ term are accurately known for at least one temperature.

c. ΔE_0° may be computed from the heats of dissociation of diatomic gases obtained from spectroscopic data. This method is discussed in Sec. 12.

From this it can be seen that, although tabulated values of the function $(F^\circ - E_0^\circ)/T$ for elements and compounds may be added and subtracted in the same way as ordinary free energies of formation are handled, the evaluation of the ΔE_0° for the reaction in question requires a somewhat special technique of computation before values for K can be derived.

In general, the problem of computing rigorously correct values for partition functions is a complicated process, requiring that every possible rotational, vibrational, and electronic energy level be taken into consideration in performing the indicated summations, due attention being paid to the use of the correct statistical weights (p 's) of the various levels. As a matter of fact, the band spectrum of a molecule containing more than two atoms is so complex that a complete picture of all the possible energy levels of the molecule that are likely to be occupied at temperatures within reason is almost out of the question. Computations of the thermodynamic functions of most diatomic molecules have already been performed when the necessary spectroscopic data were available; for more complicated molecules, it is necessary to use certain approximate methods discussed in Sec. 5. As an illustration of the use of these rigorous procedures, the heat capacity, entropy, and free energy of the simplest possible system will be performed, namely, oxygen atoms possessing only electronic levels.

4. Calculation of Atomic Thermodynamic Functions. *Illustration 1.*—The energy levels of atomic oxygen and their corresponding statistical weights are tabulated as follows, in Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., 3d sup. vol., part II, p. 777, 1935:

| Term | Frequency separation. cm.^{-1} | Statistical weight, $-p$ |
|---------|--|-----------------------------|
| 3P_2 | Ground level | 5 |
| 3P_1 | 157.4 | 3 |
| 3P_0 | 226.1 | 1 |
| 1D_2 | 15,807 | 5 |
| 1S_0 | 33,662 | 1 |

Calculate:

- The partition function at 298.1° , 1000° , and 2000°K .
- $(F^\circ - E_0^\circ)/T$ at 298.1° , 1000° , and 2000°K .

c. The standard entropy of $O_{(g)}$ at $298.1^\circ K$.

d. The heat capacity at $298.1^\circ K$.

Solution.—a. In order to compute the various terms in the Q sum, it is necessary to convert the above energies expressed in reciprocal centimeters (wave numbers) into true energy units to correspond with kT . Accordingly, the energies of the various levels above the ground level will be expressed in calories per mole; and the Boltzmann factors are then $e^{-\epsilon/RT}$ with $R = 1.987$. The energy equivalent to a given frequency may be computed from the fundamental relation between energy and mechanical frequency

$$\epsilon = h\nu, \quad (7.28)$$

where ν represents the frequency in cycles per second and h is Planck's proportionality constant (6.547×10^{-27} erg sec.). Since $c = \lambda\nu$, where c is the velocity of light (2.9977×10^{10} cm. sec.⁻¹) and λ is the wave length (centimeters) corresponding to the frequency ν , it follows that the above values for the frequency separation of the levels ($1/\lambda$) must be multiplied by c in order to convert to ν . Therefore

$$\begin{aligned} \epsilon_{(\text{cal./mole})} &= \frac{(6.547 \times 10^{-27})(2.9977 \times 10^{10})(6.064 \times 10^{23})}{4.185 \times 10^7} \omega \\ \epsilon_{(\text{cal./mole})} &= 2.844\omega, \end{aligned} \quad (7.29)$$

where ω equals the wave number in reciprocal centimeters. The tabulated energy levels in calories per mole then become:

| Term | cal./mole above ground level | Weight, $-p$ |
|---------|---------------------------------|--------------|
| 3P_2 | 0 | 5 |
| 3P_1 | 447.6 | 3 |
| 3P_0 | 643.0 | 1 |
| 1D_2 | 44,960.0 | 5 |
| 1S_0 | 95,730.0 | 1 |

The Q sum may now be computed from these values of ϵ and p at the required temperatures:

$$Q_{298.1} = 5 + 3e^{-447.6/592.3} + e^{-643.0/592.3} + 5e^{-44,960/592.3} + e^{-95,730/592.3}.$$

Inspection of this series shows that, since the first term is 5 and the exponents of the last two terms are larger than 7 at all required temperatures, the contribution of these two levels to Q is negligible. Hence,

$$Q_{298.1} = 5 + 3(0.470) + 0.338 = 6.748.$$

$$Q_{1,000} = 5 + 3e^{-447.6/1,987} + e^{-643.0/1,987} = 5 + 2.397 + 0.723 = 8.120.$$

$$Q_{2,000} = 5 + 3e^{-447.6/3,974} + e^{-643/3,974} = 5 + 2.679 + 0.850 = 8.529.$$

b. The value of $(F^\circ - E_0^\circ)/T$ for $O_{(g)}$ at 1 atm. may be computed for these three temperatures from Eq. (7.21):

$$\frac{F^\circ - E_0^\circ}{T} = -6.863 \log 16 - 11.438 \log T - 4.575 \log Q + 7.267.$$

$$\frac{F^\circ - E_0^\circ}{T} = -11.438 \log T - 4.575 \log Q - 0.996.$$

$$\left(\frac{F^\circ - E_0^\circ}{T}\right)_{298.1} = -11.438 \log 298.1 - 4.575 \log 6.748 - 0.996 = -33.171.$$

$$\left(\frac{F^\circ - E_0^\circ}{T}\right)_{1,000} = -39.475.$$

$$\left(\frac{F^\circ - E_0^\circ}{T}\right)_{2,000} = -43.056.$$

These values may then be combined with corresponding values for other molecules and used to evaluate equilibria involving oxygen atoms.

c. The entropy of $O_{(g)}$ at 298.1°K. and 1 atm. is given by the sum of (7.13) and (7.17):

$$S^\circ_{tr.} = 6.863 \log 16 + 26.00 = 34.263,$$

$$S^\circ_{int.} = R \ln Q + \frac{1}{T} \frac{\sum \epsilon p e^{-\epsilon/RT}}{Q}, \quad (7.30)$$

where the energy terms ϵ are expressed in calories per mole. Therefore

$$S^\circ_{int.} = 4.575 \log 6.748 + \left[\frac{3(447.6)(0.47) + 643(0.338)}{(298.1)(6.748)} \right] = 4.21.$$

Consequently the total entropy of $O_{(g)}$ is $S^\circ_{298.1} = 38.47$ cal./deg.

d. The heat capacity at constant pressure may be computed by adding 4.968 to Eq. (7.7). The internal heat capacity at 298.1°K. is computed from (7.7) in the form

$$C_i^\circ = \frac{1}{RT^2} \left[\frac{\sum \epsilon^2 p e^{-\epsilon/RT}}{Q} - \frac{(\sum \epsilon p e^{-\epsilon/RT})^2}{Q^2} \right], \quad (7.31)$$

where the energy levels are in calories per mole. The internal contribution at 298.1° is

$$C_i^\circ = \frac{1}{1.987(298.1)^2} \left\{ \frac{(448)^2(1.41) + (643)^2(0.338)}{6.748} - \left[\frac{(448)(1.41) + (643)(0.338)}{6.748} \right]^2 \right\}.$$

$$C_i^\circ = 0.266 \text{ cal./}(\text{mole})(\text{deg}).$$

$$C_{298.1} \text{ (total)} = 4.968 + 0.266 = 5.234 \text{ cal./}(\text{mole})(\text{deg}).$$

Examination of Eq. (7.31) discloses that, at elevated temperatures ($>1000^\circ$), the 1D_2 level will begin to contribute to the heat capacity because of the large ϵ^2 factor; hence the term $\epsilon^2 p e^{-\epsilon/RT}$ is appreciable, even though the exponential factor itself is small. However, the effect of this level on the Q sum, and hence on $(F^\circ - E_0^\circ)/T$, will still be negligible.

It is also interesting to note that the increasing value of the partition function with increasing temperature is a quantitative measure of the tendency of the oxygen atoms to populate the higher energy levels. Thus, at 298°, 1000°, and 2000°K. the mole fractions of atoms in the ground level are 0.148, 0.123, and 0.117, respectively.

The following is a brief comparison of some statistically computed entropies with the calorimetrically determined values at 298.1°K.:

| Substance | Entropy | |
|----------------|--------------|---------------|
| | Calorimetric | Spectroscopic |
| N ₂ | 45.9 | 45.788 |
| O ₂ | 49.1 | 49.03 |
| HCl | 44.5 | 44.64 |
| HBr | 47.6 | 47.48 |
| HI | 49.5 | 49.4 |

5. Approximate Methods for Evaluating Partition Functions.—

In the case of the oxygen atoms, discussed in the foregoing illustration, it was found that the calculation of the usual thermodynamic functions was a relatively simple process due to the fact that only three energy levels had to be considered, except for the heat capacity above 1000°K. when a fourth level began to contribute. However, even for simple diatomic molecules, the number of energy levels that must be taken into account when performing the various summations is vastly greater. This condition depends on the fact that at any temperature the molecules are distributed over a great many rotational, vibrational, and electronic energy levels, instead of only electronic levels as in the case of oxygen atoms. Now, as a general rule, molecules which contain no odd electrons— NO —or unpaired electrons— O_2 —possess electronic levels which are apt to be about 100,000 cal. above the nondegenerate ground level and consequently are not appreciably occupied except at very high temperatures. Spectroscopic compounds, such as CH , NH , and OH , possess low-lying electronic levels and degenerate ground states ($p_0 > 1$), but it is usually safe to assume that the electronic states of ordinary molecules are so high that they do not contribute significantly to the usual thermodynamic functions and hence may be disregarded.

On the other hand, the separation of rotational levels is of the order of 20 cal./mole, and the separation of vibrational levels is of the order of 3,000 cal./mole; consequently these levels contribute appreciably to the partition function at ordinary temperatures. Thus, the partition-function method of obtaining thermodynamic functions of polyatomic molecules depends primarily on the evaluation of the distribution of molecules over available rotational and vibrational states at a given temperature, and the energy absorption, accompanying the redistribution of the molecules over these levels, at a slightly higher temperature. The procedure has already been described in detail in Sec. 2; but owing to the great multiplicity of rotational-vibrational states in polyatomic molecules, approximate values for partition functions are usually computed on the basis of the two fundamental assumptions that (1) the molecule behaves as a rigid rotator (no centrifugal stretching) possessing one harmonic oscillator for each vibrational degree of freedom and (2) the partition function

for the rotational-vibrational states may be expressed as the product of the two separate functions and each may be separately computed; thus,

$$Q_{r-v.} = Q_{rot.} Q_{vib.} \quad (7.32)$$

This is tantamount to saying that the separation of the rotational levels is independent of the vibrational level, as they both are of the translational energy of the molecule. Actually this is not the case, but the resulting error in the thermodynamic calculations does not appear to be serious. Hence these functions may be computed from the equations

$$Q_{rot.} = \Sigma p_r e^{-\epsilon_r/RT}. \quad (7.33)$$

$$Q_{vib.} = \Sigma p_v e^{-\epsilon_v/RT}. \quad (7.34)$$

The problem is therefore to evaluate the statistical weights and energies of the rotational levels and the statistical weights and energies of the vibrational levels of polyatomic molecules.

(A) ROTATIONAL PARTITION FUNCTIONS. *Case 1. Diatomic and Linear Molecules.*—It is known from quantum mechanics that a rigid diatomic molecule possessing two equal moments of inertia can exist in a series of rotational states possessing the energies

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1), \quad (7.35)$$

where J is an integer, called the rotational quantum number, which may assume the values 0, 1, 2, The physical significance of J is that it is a quantitative measure of the total angular momentum of the molecule in the various rotational states. I is the moment of inertia of the molecule with respect to two mutually perpendicular axes which are located at the center of gravity of the molecule and are perpendicular to its axis. This equation is also approximately true for linear polyatomic molecules, *e.g.*, CO_2 , although in such cases a second quantum number depending on the angular momentum of the nuclear vibrations of the molecule should be introduced.³

The statistical weights of the rotational levels of diatomic molecules which do not possess nuclear spin are given by the relation

$$p_J = 2J + 1.$$

Thus the level, characterized by the number 3, actually consists of seven practically indistinguishable rotational levels. If both nuclei are identical, alternate p 's are zero; that is, every other rotational level is missing and, in computing the Q sum, this fact must be taken into consideration. However, it will be seen shortly that factors of this sort are conveniently handled by dividing the approximate rotational state sum by a factor possessing definite geometrical significance, called the "symmetry number." In general, the statistical weights of the rotational levels of diatomic molecules are only given by $2J + 1$ with $J = 0, 1, 2, 3, \dots$ when the molecule contains electrons in completed groups ($^1\Sigma$ molecules). Nevertheless, the weights can still be expressed by $2J + 1$ when the necessary modifications in J are recalled and the rotational partition function is given by the sum over all possible levels:

$$Q = \sum_{J=0}^{\infty} (2J + 1) e^{-h^2 J(J+1)/8\pi^2 I k T} = \sum_{J=0}^{\infty} (2J + 1) e^{-\sigma J(J+1)} \quad (7.36)$$

where

$$\sigma = \frac{h^2}{8\pi^2 I k T}. \quad (7.37)$$

The sum expressed by Eq. (7.36) may be replaced by an integral, when σ is small,⁴ and integrated to give

$$Q = \frac{1}{\sigma} + \frac{1}{4} + \dots \quad (7.38)$$

For all practical purposes, the first term is the only one that need be considered; hence

$$Q_R = \frac{1}{\sigma} = \frac{8\pi^2 I k T}{h^2}, \quad (7.39)$$

where I is the moment of inertia of the molecule, k is the Boltzmann constant, and h is Planck's constant. Equation (7.39) may also be employed to compute the rotational partition functions of linear molecules, such as CO_2 , CS_2 , and HCN , with a good degree of approximation.

Case 2. Spherical Rotator.—A molecule, such as CH_4 , considered as a rigid rotator with three equal moments of inertia, possesses rotational energy levels given by Eq. (7.35); but the

statistical weights are in this case equal to $(2J + 1)^2$. The partition function is, therefore,

$$Q = \sum_{J=0}^{\infty} (2J + 1)^2 e^{-\sigma J(J+1)}, \quad (7.40)$$

where σ has the same significance as in Eq. (7.37). When the Q sum is replaced by an integral, as in the case of the diatomic molecule,⁴ the approximate result

$$Q = \sqrt{\pi} \sigma^{-3/2} \left(1 + \frac{\sigma}{4} + \cdots \right) \quad (7.41)$$

is obtained. Here again, when σ is small, only the first term need be considered, and therefore

$$Q_R = \frac{\sqrt{\pi}}{\sigma^{3/2}} = \sqrt{\pi} \left(\frac{8\pi^2 I k T}{h^2} \right)^{3/2}. \quad (7.42)$$

Case 3. Symmetrical Top.—Molecules possessing a pyramidal configuration, such as ammonia, have two equal moments of inertia and a third distinct moment with respect to the axis of symmetry. The rotational energy levels are known from quantum mechanics to be given by the equation

$$E = \frac{h^2}{8\pi^2 I} \left[J(J + 1) + \left(\frac{I}{I'} - 1 \right) K^2 \right], \quad (7.43)$$

where I' is the moment of inertia with respect to the axis of symmetry, and K is a second rotational quantum number which can be equal to or less than J in absolute value but not greater. Thus each rotational level is characterized by two integers, and each level has a weight of $2J + 1$. However, in this case the integration is further complicated by the fact that each of the $2J + 1$ sublevels has a further degeneracy of $2J + 1$ imposed on it by the quantum number K . When the Q sum is replaced by the equivalent integral⁴ and all but the first term of the series integrand dropped, the result obtained is

$$Q_R = \frac{\sqrt{\pi}}{\sigma \sqrt{\sigma'}}, \quad (7.44)$$

where $\sigma = \frac{h^2}{8\pi^2 I k T}$ and $\sigma' = \frac{h^2}{8\pi^2 I' k T}$.

Case 4. Asymmetrical Top.—The most general type of molecular architecture is that in which the molecule has three distinct moments of inertia (H_2O , $\text{C}_2\text{H}_5\text{OH}$, etc.). In this case it is impossible to obtain simple expressions, such as (7.35) and (7.43), for the rotational levels, and, accordingly, by analogy, the approximate partition function

$$Q_R = \frac{\sqrt{\pi}}{(\sigma\sigma'\sigma'')^{1/2}} \quad (7.45)$$

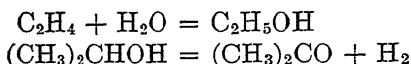
has been deduced and checked by numerical calculations. As before, the σ 's represent the functions $h^2/(8\pi^2IkT)$ corresponding to each of the three principal moments of inertia of the molecule.

Case 5.—Molecules Possessing Internal Rotational Degrees of Freedom.—It is known that when the mutual potential energy of two groups of atoms connected by a single bond is less than the equipartition value of the thermal energy associated with this bond, free or unhindered rotation of the two groups with respect to each other may occur. On the other hand, when the mutual potential energy of the two groups is substantially greater than the equipartition value, the rotation is hindered; and, if the potential energy is very large, the motion becomes a torsional oscillation about the connecting bond. Obviously, the contribution of such a degree of freedom to the internal energy, heat capacity, and entropy of the molecule will depend on whether the motion is free or hindered. There is no positive way of predicting, in advance of some experimental data on the heat capacity or the temperature dependence of the dipole moment of the substance, which type of motion is involved; indeed, unless the experimental data are unusually precise, the interpretation may still be uncertain.

Perhaps the most intensively studied case of this sort, and, at the same time, the simplest, is that of ethane. After numerous publications of a theoretical and experimental nature it appears to be well established that the rotation of the methyl groups with respect to each other is hindered by a potential barrier of 2,750 cal./mole. Pitzer⁵ has prepared tables by means of which it is possible to compute the contribution of a restricted rotational degree of freedom to the molar heat capacity and entropy when the height of the potential maxima and the reduced moment of inertia are known. Thus, in the case of ethane, since interatomic

distances and bond angles are known, Pitzer's tables offer a convenient means for extending the temperature range of the experimental data on heat capacities. These heat capacities were used in conjunction with the known vibration frequencies to establish the height of the potential barrier (2,750 cal.).

A number of cases of assumed free rotation about C—C bonds have been treated by Eidinoff and Aston⁶ and by Kassel.⁷ Schumann and Aston have treated the gaseous equilibria^{8,9}



from the experimental and theoretical standpoint. In the case of ethyl alcohol it was necessary to assume potentials, restricting the rotation of the CH₃ and OH groups, equal to 3,000 and 10,000 cal., respectively, in order to make computed entropies agree with calorimetric values. In the case of acetone the rotation of the methyl groups is supposed to be hindered by a potential of 1,000 cal.; and in isopropyl alcohol the potentials are 3,400 and 5,000 cal. for the CH₃ and OH groups, respectively. Since in all these cases there is a great deal of uncertainty regarding the assignment of numerical values to the fundamental vibration frequencies of these molecules and since the computational labors are considerable, the treatment of internal rotations is at present of more theoretical than practical interest. Developments in this field, up to 1940, are summarized in the papers by Pitzer,¹⁰ Wilson,¹¹ and Aston.¹²

(B) THE SYMMETRY NUMBER AND NUCLEAR SPIN.—Having derived approximate Eqs. (7.39), (7.44), and (7.45) for the rotational partition functions of the various types of molecules, we can substitute these expressions into Eqs. (7.6), (7.8), (7.13), and (7.21), and compute the rotational contribution to the different thermodynamic functions. However, owing to the fact that some molecules possess identical nuclei which can be interchanged by simple rotation about an axis to produce identical states, a definite part of the rotational levels of the molecule is missing, which, from the form of the Q sum, indicates a numerically smaller value for this quantity. Thus, in the case of the O₂ molecule or the CO₂ molecule, it is possible to interchange the oxygen nuclei by a 180° rotation about the perpendicular axis through the center of gravity; hence these molecules are able to

occupy two equivalent orientations in space. These molecules are then said to have a symmetry number (s) equal to 2. Again, in the case of the ammonia molecule there are three equivalent positions which the hydrogen nuclei can occupy by rotation about the symmetry axis of the molecule; therefore the symmetry number is 3. Similarly, the three hydrogen nuclei of CH_3Cl can be interchanged by rotation and $s = 3$; but in the case of CH_3OH the symmetry number is unity, because the $\text{C}-\text{O}-\text{H}$ angle is about 110° and one complete rotation is necessary in order to regain the original state of the molecule. The symmetry numbers of such molecules as CH_4 , benzene, and *p*-dichlorobenzene are 12, 12, and 4, respectively.

An additional complication arises in the evaluation of rotational partition functions when some of the nuclei constituting the molecule possess spin momentum, since a further degeneracy is thereby imposed on the rotational levels. At temperatures above room temperature the combined effect of symmetry and nuclear spin on the rotational partition function may be evaluated by multiplying the partition functions, as given above, by the factor

$$f = \frac{(2i_1 + 1)(2i_2 + 1)(2i_3 + 1) \cdots}{s}, \quad (7.46)$$

where the i 's represent the units of spin momentum, possessed by each atom, and s is the symmetry number. The quantities in parentheses are the spin multiplicities or weights and are equivalent to a nuclear spin partition function for each atom present in the molecule.

The i values for some common atoms and the corresponding spin multiplicities are as follows:

| Atom | H | D | C | N | O | Cl |
|----------|---------------|---|---|---|---|---------------|
| i | $\frac{1}{2}$ | 1 | 0 | 1 | 0 | $\frac{5}{2}$ |
| $2i + 1$ | 2 | 3 | 1 | 3 | 1 | 6 |

Thus, in the case of O_2 or CO_2 the partition function computed by means of Eq. (7.39) should be multiplied by the factor $\frac{1}{2}$. The partition function for NH_3 should be multiplied by $(3 \times 2 \times 2 \times 2)/3 = 8$ and the partition function for CH_3Cl should be multiplied $(2^3 \times 6)/3 = 16$.

From Eq. (7.13), the total rotational entropy, including nuclear spin entropy, would be

$$S_R^\circ = R \ln f Q_R + RT \frac{d \ln f Q_R}{dT} = R \ln f + R \ln Q_R + RT \frac{d \ln Q_R}{dT}; \quad (7.47)$$

consequently the effect of nuclear spin and symmetry on the entropy is to contribute the additive term $R \ln f$, where f is defined by Eq. (7.46).

Now, it has been shown by Gibson and Heitler¹³ that nuclear spin effects carry through intact in chemical reactions at ordinary and high temperatures or, in other words, a given atom possesses the same amount of spin regardless of its state of chemical combination. Consequently the same nuclear spin contributions to the partition functions will be found on both sides of a chemical or thermodynamic equation and may be disregarded for all practical purposes. This has led to the system of recording so-called virtual or practical entropies, which are simply total entropies less spin entropies and are the values to be employed in thermochemical calculations. Some tabulations of entropies contain values for total entropies; and it is important that all values used be converted to either total entropies or virtual entropies. In any case, the symmetry number must always be used, and the rotational partition functions to be substituted in Eqs. (7.6), (7.8), (7.13), and (7.21) are given by Q_R/s , where Q_R is the value computed from the moments of inertia of the molecule.

(C) SUMMARY OF EQUATIONS FOR ROTATIONAL HEAT CAPACITIES AND ENTROPIES.—With the exception of hydrogen and deuterium, gases acquire the equipartition value, $RT/2$, for the kinetic energy associated with each rotational degree of freedom at low temperatures ($< 50^\circ\text{K.}$); hence the rotational heat capacity is R cal./ (mole)(deg.) for diatomic or linear molecules and $\frac{3}{2}R$ for polyatomic molecules possessing three rotational degrees of freedom.

The following equations are obtained for the rotational entropies of molecules, treated as rigid rotators, when the values for the partition functions given by Eqs. (7.39), (7.42), (7.44), and (7.45) are substituted in (7.13) ($P = 1$ atm.).

Diatomic or linear rotator:

$$S_R^\circ = R \ln IT + 177.676 - R \ln s, \quad (7.48)$$

where s is the symmetry number. At 298.1°K. this becomes

$$S_{298.1}^\circ = 4.575 \log I - 4.575 \log s + 188.996. \quad (7.49)$$

Spherical rotator, symmetric top, or asymmetric top:

$$S_R^\circ = \frac{R}{2} \ln II'I'' + \frac{3}{2} R \ln T - R \ln s + 267.649, \quad (7.50)$$

where $I = I' = I''$ for the spherical rotator, $I = I' \neq I''$ for the symmetric top, and $I \neq I' \neq I''$ for the asymmetric top. At 298.1°K. this becomes

$$S_{298.1}^\circ = 2.288 \log II'I'' - 4.575 \log s + 284.631. \quad (7.51)$$

The moments of inertia required to evaluate rotational entropies are obtained either from the spacing of the rotational lines in the infrared spectrum of the molecule or, more generally, from data on interatomic distances and bond angles, obtained from the electron diffraction pattern of the molecule.

(D) VIBRATIONAL PARTITION FUNCTIONS.—As mentioned in the introduction to Sec. 5, the approximate evaluation of rotation-vibration partition functions of gases is based on the assumption that each vibrational degree of freedom is equivalent to an harmonic oscillator. If the molecule consists of n atoms, it possesses a total of $3n$ degrees of freedom, of which $3n - 5$ or $3n - 6$ are vibrational degrees of freedom, depending on whether the molecule has two or three moments of inertia. The problem is, therefore, to compute the partition function for each of the $3n - 6$ harmonic oscillators, since the product of the individual partition functions is, to a good degree of approximation, equal to the total vibrational partition function for the molecule as a whole.

It is known from quantum theory that the energy levels of an harmonic oscillator are given by the relation

$$E_v = (v + \frac{1}{2})h\nu, \quad (7.52)$$

where $v = 0, 1, 2, \dots$, and ν is the fundamental vibration frequency in cycles per second. From this equation it will be seen that, even in the lowest vibrational state ($v = 0$), the harmonic oscillator retains the half quantum of vibrational

energy ($h\nu/2$), called the "zero-point vibrational energy." Depending on the magnitude of ν and the temperature, the molecules are distributed over the different levels of the oscillator for which $v = 0, 1, 2$, etc., where each level has a statistical weight of unity. Hence the partition function for the i th harmonic oscillator corresponding to one vibrational degree of freedom is given by the equation

$$Q_i = e^{-(0+\frac{1}{2})h\nu/kT} + e^{-(1+\frac{1}{2})h\nu/kT} + e^{-(2+\frac{1}{2})h\nu/kT} + \dots \quad (7.53)$$

$$= e^{-h\nu/2kT}(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots), \quad (7.54)$$

or the partition function for the vibrational energy, in excess of the zero-point vibrational energy, is

$$Q_i = 1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + \dots = \frac{1}{1 - e^{-h\nu/kT}}. \quad (7.55)$$

The heat capacity associated with the i th vibrational degree of freedom may be evaluated by substituting Q_i in (7.8) and performing the indicated differentiations. The heat capacity associated with a mole of harmonic oscillators of fundamental frequency ν is, therefore,

$$c_i^\circ = RE(x_i) = \frac{Rx^2e^x}{(e^x - 1)^2}, \quad (7.56)$$

where $x_i = \frac{h\nu_i}{kT}$.

The entropy associated with the frequency ν_i is obtained by substituting Eq. (7.55) in (7.13). The vibrational entropy per mole is, therefore,

$$s_i^\circ = R \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right]. \quad (7.57)$$

The total vibrational heat capacity and entropy associated with the vibrational degrees of freedom will then be the sum of the values computed from Eqs. (7.56) and (7.57) for each frequency. It will be noted that c_i° and s_i° are functions of a single variable x , where x equals θ/T and θ is a constant for a given frequency ($h\nu/k$). Accordingly, tables of numerical values have been prepared for the three different functions involved in Eqs. (7.56) and (7.57), corresponding to a practical range of values for x . Consequently, from the known frequency ν it is only necessary to calculate θ , and then x may be calculated

at the desired temperatures and the corresponding values of the required functions read from these tables. A set of such tables of Einstein functions is included in Appendix 2. These tables have been computed for oscillators possessing the frequency ν along three different directions; hence one-third the recorded value should be used for a single vibrational degree of freedom.

The problem of evaluating the fundamental vibration frequencies corresponding to each vibrational degree of freedom, or, more correctly, to each normal mode of vibration of the molecule, is a complicated dynamical problem, the complexity of which increases rapidly with the number of atoms in the molecule. The frequencies are observed in either the infrared or Raman spectrum of the molecule, or possibly both types of spectra. For transitions to be able to occur from one energy level under the influence of infrared radiation or Raman radiation, it is necessary that the mode of vibration satisfy certain definite rules regarding the change of electric moment or polarizability of the molecule associated with the vibration. These rules have been developed as a result of the study of the symmetry properties of the different types of molecules, in conjunction with group theory. Applications of these rules make it possible to determine which of all the frequencies observed in the infrared and Raman spectrum of a molecule are fundamental frequencies and not overtones or combination frequencies. The process of evaluating the fundamental frequencies for polyatomic molecules is a difficult and important one, since the accuracy of the thermodynamic calculations depends on the correctness of assignment of numerical values to these fundamentals.

From the standpoint of most thermochemical calculations it is very often possible to make rough assignments of fundamental frequencies by dividing the total vibrational degrees of freedom into stretching or valence vibrations, corresponding to the motion of atoms along the line connecting the two atoms, and bending or deformation frequencies, corresponding to the motion of atoms resulting in the deformation of bond angles. If the molecule contains n atoms, there will obviously be $n - 1$ valence vibrations; the remaining vibrational degrees of freedom are then ascribed to deformation vibrations. This method of assigning a vibrational degree of freedom to a definite chemical bond is dynamically incorrect, but in many cases it appears as though the bulk of the motion, and hence the energy of a mode of vibra-

tion, resides in a particular bond. For example, all compounds containing carbon and hydrogen atoms exhibit frequencies around $3,000\text{ cm.}^{-1}$ and $1,400\text{ cm.}^{-1}$; consequently, it is believed that the first frequency is due to vibrations along the C—H bond and the second frequency is due to deformations of the H—C—H angle. Again, the spectra of compounds containing the hydroxyl group exhibit a frequency of about $3,500\text{ cm.}^{-1}$, the exact value depending largely on the state of dilution of the hydroxyl compound. This frequency is believed to be due to vibrations along the O—H bond. Accordingly, by examining the spectra of molecules containing one new bond at a time, it is possible to build up a series of frequency values more or less characteristic of each chemical bond, which are useful in estimating heat capacities or even rough values for entropies, where experimental data are not available. It should be emphasized that the foregoing discussion applies to molecules in the gaseous state, there being some modification (usually decreasing) of characteristic frequencies on passing from the gaseous to the liquid to the solid state.

Although a molecule may possess $3n - 5$ or $3n - 6$ vibrational degrees of freedom, there will not, in general, be that number of distinct fundamental frequencies, since the nuclear displacements that constitute the vibration may occur with the same frequency in more than one direction. Such vibrations are spoken of as multiple or degenerate vibrations. As an example of this phenomenon the deformation or perpendicular vibration of the linear molecule $\text{O}=\text{C}=\text{O}$ can take place in such a manner that the two oxygen atoms vibrate up and down simultaneously with a corresponding up-and-down motion of the carbon atom, all in the plane of the page. However, the identical motion may occur in a plane at right angles to this page and hence the corresponding frequency is doubly degenerate; in computing thermodynamic functions, the numerical contribution of this frequency is doubled. The higher the degree of symmetry of the molecule, the greater the degree of degeneracy of the fundamental frequencies, as is illustrated by the multiply degenerate frequencies exhibited by organic molecules. For an interesting, elementary introduction to the theoretical and laboratory technique of this subject, the short monograph by Sutherland, "Infra-Red and Raman Spectra,"¹⁴ should be consulted.

6. Calculation of the Entropy and Heat Capacity of Ethylene.

Illustration 2.—The spectrum of the ethylene molecule has been analyzed by Bonner,¹⁵ and the following assignment of fundamental frequencies made:

$$\begin{array}{ll} \omega_1 = 1,623 \text{ cm.}^{-1} & \omega_7 = 950 \text{ cm.}^{-1} \\ \omega_2 = 3,019 & \omega_8 = 3,107 \\ \omega_3 = 1,342 & \omega_9 = 950 \\ \omega_4 = 2,988 & \omega_{10} = 940 \\ \omega_5 = 1,444 & \omega_{11} = 1,100 \\ \omega_6 = 3,069 & \omega_{12} = 825 \end{array}$$

Badger¹⁶ has deduced the following values for the principal moments of inertia of the molecule from its band spectrum:

$$I = 33.2 \times 10^{-40} \text{ g. cm.}^2 \quad I' = 27.5 \times 10^{-40} \quad I'' = 5.7 \times 10^{-40}.$$

Calculate:

- The molar translational entropy of $\text{C}_2\text{H}_{4(g)}$ at 298.1°K. and 1 atm. pressure.
- The rotational entropy at 298.1°K.
- The vibrational entropy at 298.1°K.
- The total entropy of ethylene at 298.1°K. and 1 atm. in the ideal gas state and the actual gas state.
- The heat capacity of $\text{C}_2\text{H}_{4(g)}$ as a function of temperature in the range 300 to 1300°K.

Solution.—*a.* The molecular weight of ethylene is 28.052 and the translational entropy at 298.1° [Eq. (7.17)] is, therefore,

$$S_{\text{tr.}}^\circ = 6.863 \log 28.052 + 26.00 = 35.94 \text{ cal./}(\text{mole})(\text{deg.}).$$

b. The equation for computing the rotational entropy of an asymmetric top is (7.51)

$$S_R^\circ = 2.288 \log II'I'' - 4.575 \log s + 284.631.$$

In order to evaluate the symmetry number of the planar C_2H_4 molecule, it should be noted that three successive rotations of the molecule will cause each H atom to occupy four distinct but equivalent orientations in space, and therefore $s = 4$.

$$S_R^\circ = 2.288 \log (33.2)(27.5)(5.7)10^{-120} - 4.575 \log 4 + 284.631 = 15.87 \text{ units.}$$

c. The vibrational entropy at 298.1° may be evaluated by computing the function θ , corresponding to each frequency,

and reading the value $\theta/298.1$ from Tables E-2 and E-3 of Appendix 2.

To convert ω in reciprocal centimeters to $\theta = h\nu/k$, it is necessary to multiply ω by c to convert to ν and multiply by h/k . The conversion factor is, therefore,

$$\frac{hc}{k} = \frac{(6.547 \times 10^{-27})(2.9977 \times 10^{10})}{1.371 \times 10^{-16}} = 1.432.$$

The necessary data for obtaining the vibrational entropy are recorded in Table 1. The last column, headed s_i° , contains the vibrational entropy associated with the given frequency.

TABLE 1.—THE VIBRATIONAL ENTROPY OF $C_2H_4(g)$ AT 298.1°K.

| $\omega, \text{cm.}^{-1}$ | θ | $x = \frac{\theta}{298.1}$ | $\frac{Rx}{e^x - 1}$ | $-R \ln (1 - e^{-x})$ | s_i° |
|---------------------------|----------|----------------------------|----------------------|-----------------------|-------------|
| 1,623 | 2,326 | 7.804 | 0.0063 | 0.0003 | 0.0066 |
| 3,019 | 4,327 | 14.515 | 0 | 0 | 0 |
| 1,342 | 1,924 | 6.454 | 0.0202 | 0.0022 | 0.0224 |
| 2,988 | 4,282 | 14.366 | 0 | 0 | 0 |
| 1,444 | 2,069 | 6.942 | 0.0133 | 0.0010 | 0.0143 |
| 3,069 | 4,398 | 14.754 | 0 | 0 | 0 |
| (2)950 | 1,361 | 4.567 | 0.1906 | 0.040 | 0.2306 |
| 3,107 | 4,453 | 14.939 | 0 | 0 | 0 |
| 940 | 1,347 | 4.519 | 0.0990 | 0.021 | 0.120 |
| 1,100 | 1,576 | 5.288 | 0.0533 | 0.010 | 0.0633 |
| 825 | 1,182 | 3.966 | 0.152 | 0.0370 | 0.1890 |
| Total S_v° | | | | | 0.646 |

The total entropy at 298.1° of $C_2H_4(g)$ at 1 atm. in the ideal gas state = $35.94 + 15.87 + 0.646 = 52.46$ cal./ (mole)(deg.). It is interesting to note that the vibrational entropy is only 1.2 per cent of the total. The calorimetric value obtained by Egan and Kemp¹⁷ is 52.48 units. This value may be corrected to the actual gas at 1 atm. and 298.1° from the relation (L-R, p. 133)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \quad (7.58)$$

in conjunction with the Berthelot equation of state [Eq. (2.19)]. This gives

$$\frac{\partial S}{\partial P} = -\frac{R}{P} - \frac{27 RT_c^3}{32 P_c T^3} \quad (7.59)$$

But, since $(-R/P) = (\partial S/\partial P)$ for an ideal gas

$$\left(\frac{\partial S}{\partial P}\right)_{\text{act.}} = \left(\frac{\partial S}{\partial P}\right)_{\text{ideal}} - \frac{27}{32} \frac{RT_c^3}{P_c T^3} \quad (7.60)$$

$$\frac{\partial(S_a - S_i)}{\partial P} = -\frac{27}{32} \frac{RT_c^3}{P_c T^3} \quad (7.61)$$

Therefore

$$S_{\text{act.}} = S_{\text{ideal}} - \frac{27}{32} \frac{RT_c^3 P}{P_c T^3} \quad (7.62)$$

$$S_{\text{act.}} = 52.46 - \frac{27}{32} \frac{(1.987)}{(298.1)^3} \left(\frac{(282.8)^3}{50.9} \right) = 52.46 - 0.028$$

= 52.43 units.

d. The heat capacity of $\text{C}_2\text{H}_{4(g)}$ at constant pressure may be computed by adding the vibrational contribution, due to each frequency, to the equipartition value for translation plus rotation; thus

$$C_p = \frac{3}{2}R + \frac{3}{2}R + R + \Sigma C_v = 7.95 + \Sigma C_v. \quad (7.63)$$

Values for C_v corresponding to each frequency may be read from Table E-1. These values must be divided by three for vibrations of one degree of freedom. In order to reduce the labor of the computations, the three frequencies at 3,019, 3,069, and 3,107 have been lumped into a triply degenerate frequency at 3,065 cm^{-1} . A complete set of data is included in the Table 2 for 300°K. and 1300°K., by way of illustration, and the total computed C_p 's for other temperatures are recorded in the following:

TABLE 2.—THE HEAT CAPACITY OF $\text{C}_2\text{H}_{4(g)}$ AT CONSTANT PRESSURE

| ω | θ | $T = 300^\circ\text{K.}$ | | $T = 1300^\circ\text{K.}$ | |
|--------------------|----------|--------------------------|--------|---------------------------|--------|
| | | θ/T | C_v | θ/T | C_v |
| 1,623 | 2,326 | 7.755 | 0.0513 | 1.790 | 1.532 |
| 3,065(3) | 4,393 | 14.642 | 0 | 3.379 | 2.485 |
| 1,342 | 1,924 | 6.413 | 0.134 | 1.480 | 1.661 |
| 2,988 | 4,282 | 14.275 | 0 | 3.294 | 0.863 |
| 1,444 | 2,069 | 6.898 | 0.0953 | 1.592 | 1.616 |
| 950(2) | 1,361 | 4.538 | 0.894 | 1.047 | 3.629 |
| 940 | 1,347 | 4.490 | 0.459 | 1.036 | 1.818 |
| 1,100 | 1,576 | 5.255 | 0.290 | 1.213 | 1.760 |
| 825 | 1,182 | 3.941 | 0.624 | 0.909 | 1.855 |
| ΣC_v | | | 2.548 | | 17.219 |
| C_p | | | 10.50 | | 25.17 |

Additional computed values:

| $T^{\circ}\text{K.}$ | 500 | 700 | 900 | 1,100 | |
|----------------------|-------|-------|-------|-------|--|
| C_p | 15.21 | 18.81 | 21.51 | 23.58 | |

The foregoing calculated C_p 's may be expressed by means of the equation

$$C_p = 3.075 + 2.91 \times 10^{-2}T - 9.48 \times 10^{-6}T^2. \quad (7.64)$$

It is interesting to compare the contributions of the individual frequencies at the two temperatures. At 300° , the 3,065 frequency, which is equivalent to 8,740 cal./mole, contributes nothing to the heat capacity, since the first vibrational level is too high to be appreciably occupied at ordinary temperatures. At 1300° , this vibration is excited and contributes about 0.82 cal./(mole)(deg.). On the other hand, even at 300° , the 825 frequency (2,350 cal.) contributes 0.624 cal. to the heat capacity; at 1300° it is practically excited to the equipartition value (R) for an harmonic oscillator.

7. Estimation of Free Energy from Molecular Structure Data. Although the vibrational entropy of ethylene represents only 1.2 per cent of the total at 298° , molecules containing heavy atoms usually possess low frequency fundamentals, which make larger contributions to the heat capacity and entropy even at ordinary temperatures. In general, however, the translational plus rotational entropy is much larger than the vibrational entropy—a fact that permits the estimation of at least workable values for entropies when interatomic distances are known, but not the fundamental vibration frequencies. The treatment is illustrated by the following problem:

Illustration 3.—The electron diffraction pattern of SCl_2 indicates S—Cl distances of 2\AA and a Cl—S—Cl angle equal to 102° . Estimate (a) the standard entropy of $\text{SCl}_{2(g)}$ at 298.1°K. , and (b) the free energy of formation at 298.1°K.

Solution.—*a.* The problem is to compute the translational entropy of SCl_2 from the molecular weight (102.98), and the rotational entropy from the interatomic distances and the atomic masses. The problem of estimating the vibrational entropy is hazardous, but can be attempted, at least.

At 298.1°K. and 1 atm.,

$$S_{tr.} = 6.863 \log (102.98) + 26.00 = 39.81.$$

The principal moments of inertia may be computed as follows:

If the SCl_2 molecule is referred to xy -axes, with the center of gravity at the origin and the S atom on the $-y$ axis; then the x -coordinate of the S atom is zero and of the two Cl atoms, $\pm 2 \times 10^{-8} \sin 51^\circ = 1.554 \times 10^{-8}$ cm. The y -coordinates of the 2Cl atoms are equal; therefore, only two equations are required to obtain the y -coordinates of the Cl atoms and the S atom. They are

$$y_{\text{Cl}} - y_{\text{S}} = 2 \times 10^{-8} \cos 51^\circ = 1.258 \times 10^{-8} \text{ cm.}$$

and, since the center of gravity is at $y = 0$,

$$\bar{y} = 0 = \frac{\Sigma my}{\Sigma m} = 2(5.85 \times 10^{-23})y_{\text{Cl}} + 5.29 \times 10^{-23}y_{\text{S}}.$$

Solving these two equations gives

$$y_{\text{Cl}} = 0.392 \times 10^{-8}$$

and

$$y_{\text{S}} = -0.867 \times 10^{-8}.$$

Consequently

$$I_y = \Sigma mx^2 = 2.82 \times 10^{-38} \text{ g. cm.}^2$$

$$I_x = \Sigma my^2 = 0.577 \times 10^{-38} \text{ g. cm.}^2$$

And for a planar molecule, $I_z = I_x + I_y = 3.40 \times 10^{-38}$.

The moments of inertia to be substituted in the thermodynamic equations are the principal moments or the moments referred to the principal axes. These are axes located at the center of gravity of the molecule, about which free rotation can occur. The condition for free rotation is that the deflection moments vanish, *i.e.*, $\Sigma m(xy) = \Sigma m(xz) = \Sigma m(yz) = 0$. For this molecule all z -coordinates are zero, and it is only necessary that $\Sigma m(xy) = 0$. Substituting the above masses and coordinates shows that, for the axes as chosen, $\Sigma m(xy)$ reduces to zero; hence these are principal axes, and the computed moments are the correct ones for calculating the rotational entropy.

The symmetry number is 2 and, therefore,

$$S_R = 2.288 \log (2.82)(0.577)(3.40) \times 10^{-114} - 4.575 \log 2 \\ + 284.631 = 24.12 \text{ units.}$$

In the absence of data on the fundamental vibration frequencies of SCl_2 , the simplest procedure would be to guess about two units for the vibrational entropy and add this to the 63.93 for translation plus rotation, giving a rounded estimate of 66 cal./ (mole)(deg.) for the entropy at 298.1°K. Another method would be to guess that the three fundamentals for SCl_2 would lie somewhere in the range of the fundamentals reported by Morino and Mizushima¹⁸ for the S_2Cl_2 molecule, *i.e.*, 536, 445, 242, 208, and 104 cm^{-1} . Thus, if the values 550, 400, and 150 cm^{-1} are guessed at for SCl_2 , the vibrational contribution would be 4.19 units, giving a total of 68.12 units. This value is probably correct within ± 2 units.

b. Using the entropy values $S_{\text{SCl}_2} = 68.12$, $S_s = 7.62$, and $S_{\text{Cl}_2} = 53.31$, in conjunction with the heat of formation $-8,150$, for SCl_2 —estimated in illustration 4, Chap. IV—the standard free energy of formation is found to be

$$\Delta F^\circ = -8,150 - 298.1(7.19) = -10,290 \text{ cal.}$$

It is impossible to estimate the uncertainty of this value. The uncertainty introduced by the estimated entropy is probably about 600 cal., which is, doubtless, less than the uncertainty introduced by the estimated heat of formation.

Although the computation of the principal moments of inertia for simple, symmetrical molecules, such as SCl_2 , is a relatively easy process, the problem becomes quite complex for the general three-dimensional molecule. When the center of gravity of the molecule has been determined by either mechanical or algebraic means and a rectangular system of coordinate axes erected at that point, the coordinates of each atom referred to this system are determined and the various moments and products of inertia computed. The principal moments of inertia are then given by the roots of the cubic secular equation.¹⁹

$$\begin{vmatrix} \Sigma m(y^2 + z^2) - I & \Sigma mxy & \Sigma mxz \\ \Sigma mxy & \Sigma m(z^2 + x^2) - I & \Sigma myz \\ \Sigma mxz & \Sigma myz & \Sigma m(x^2 + y^2) - I \end{vmatrix} = 0. \quad (7.65)$$

8. Solids.—Two essentially distinct fundamental theories have been devised for predicting the energy content, and hence the

thermochemical constants, of solid bodies. The fundamentals of the Debye theory have already been briefly discussed in Chap. II, and the elements of the Einstein theory have been presented in the treatment of the vibrational energy of gaseous molecules. The Einstein theory for solids was inadequate, because, unlike gases, the harmonic oscillators, which were supposed to represent the motions taking place in the crystal lattice, were not independent but were coupled owing to their close proximity; consequently the expression $(v + \frac{1}{2})h\nu$ for the energy levels of the actual oscillations is an oversimplification.

Since both theories applied to idealized types of solids, it is not surprising that a useful theory of real crystalline bodies is in reality a combination of the two theories. It should be pointed out in advance that the far-reaching and accurate thermodynamic developments of the gaseous state have not been duplicated thus far by any of the theories for solids. In fact, the chief use of these theories has been as a tool in the extrapolation of low-temperature specific-heat data down to the absolute zero in the experimental determination of third-law entropies. The treatment for real crystalline solids is essentially the one due to Born and Von Kármán,^{20,p.322} but the actual computational procedure employed depends on whether the lattice of the solid under consideration is an atomic lattice (metal halides, oxides, etc.) or a molecular lattice (CO₂, benzene, etc.).

The following considerations indicate, in a rough way, the essential difference between the two cases. When an atomic lattice absorbs heat energy at constant volume, atoms undergo limited translational displacements about their equilibrium positions with components along the x -, y -, z -axes. As the disturbance is propagated from atom to atom, the pattern of motion resembles a compressional wave with three different velocities of propagation along the three axes, since, unless the solid is an element, it will in general be anisotropic. The heat capacity associated with such motions is assumed by Born and Von Kármán to be represented by three Debye functions $D(x_1)$, $D(x_2)$, $D(x_3)$, characteristic of the lattice, in addition to the heat capacity associated with the oscillations of the atoms with respect to one another. If the molecule contains p atoms, there will be $p - 1$ of such interactions, and each of these oscillations will, in general, possess three degrees of freedom. Since, however,

individual molecules do not exist as such in the crystal lattice, these frequencies are not identifiable with the internal vibrations of the molecule in the gaseous state and are not determined by spectroscopic means. The heat capacity associated with these $p - 1$ oscillations is assumed to be represented by Einstein functions and, consequently, the total molar-heat capacity of the atomic lattice is given by the equation

$$C_v = R\{D(x_1) + D(x_2) + D(x_3) + (p - 1)[E(x_1) + E(x_2) + E(x_3)]\}, \quad (7.66)$$

where there are $p - 1$ distinct sets of characteristic Einstein functions to be considered in evaluating C_v .

For the purpose of numerical calculations where the characteristic Debye and Einstein functions must be determined by "fitting" the available low-temperature heat-capacity data, Kelley²¹ uses a single Debye function as a sort of average of the three functions along the three coordinate axes, and, similarly, a single average Einstein term is used for each of the $p - 1$ oscillations. Therefore

$$C_v = \left[D(x) + \sum_{i=1}^{p-1} E(x_i) \right] 3R, \quad (7.67)$$

where

$$D(x) = D\left(\frac{h\nu_D}{kT}\right) = D\left(\frac{\theta_D}{T}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2} \quad (7.68)$$

and

$$E(x) = E\left(\frac{h\nu}{kT}\right) = E\left(\frac{\theta}{T}\right) = \frac{x^2 e^x}{(e^x - 1)^2}. \quad (7.69)$$

In Eq. (7.68), ν_D represents the limiting frequency in the Debye spectrum of frequencies possessed by the lattice, whereas ν is one of the $p - 1$ frequencies characteristic of the oscillations of the atoms with respect to each other. Values for both of these functions may be obtained from tables in Appendixes 2, 3, when x is known. At low temperatures, where T/θ_D is of the order of 0.1, Eq. (7.68) may be integrated^{20,p.324} giving

$$D\left(\frac{\theta_D}{T}\right) = 77.7 \left(\frac{T}{\theta_D}\right)^3. \quad (7.70)$$

9. Evaluation of Entropy from Heat Capacity Data. *Illustration 4.*—The following values for the heat capacity of NiO

have been calorimetrically determined by Seltz, DeWitt, and McDonald:²²

| Temperature, °K. | C_p , cal./mole | Temperature, °K. | C_p , cal./mole |
|------------------|-------------------|------------------|-------------------|
| 68.05 | 1.607 | 150.08 | 5.93 |
| 78.19 | 2.185 | 162.37 | 6.54 |
| 85.89 | 2.625 | 172.61 | 7.02 |
| 94.42 | 3.094 | 183.01 | 7.50 |
| 103.13 | 3.693 | 204.20 | 8.12 |
| 115.71 | 4.242 | 225.34 | 8.84 |
| 131.10 | 5.00 | 247.81 | 9.52 |
| 141.72 | 5.58 | 286.32 | 10.43 |
| | | 296.68 | 10.56 |

Compute the entropy of NiO at 298.1°K.

Solution.—The problem is to compute the entropy between 68 and 298.1°K. by graphical integration of the above data and to estimate the contribution between 0 and 68°K. by means of the modified Born-Von Kármán theory of heat capacities. Since NiO contains only two atoms, Eq. (7.67) becomes

$$C_v = 3R[D(x) + E(x)] = 3R \left[D\left(\frac{\theta_D}{T}\right) + E\left(\frac{\theta_E}{T}\right) \right].$$

As a first approximation, assume $\theta_D = \theta_E$, $C_p = C_v$, and use the heat capacity at 68°K. in order to locate a rough value for θ_D ; therefore

$$1.607 = 6R \left(\frac{\theta_D}{68.05} \right) \quad \text{or} \quad 3R \left(\frac{\theta_D}{68.05} \right) = 0.804.$$

From Table D-1, Appendix 3, this value of C_v corresponds to $\theta_D/68.05 = 8.15$, or $\theta_D = 554$. As a general rule, $\theta_E > \theta_D$; and in residual ray calculations on diatomic molecules, it is customary to assume that $\theta_E = 1.35\theta_D$. Consequently, as a second approximation, $\theta_D = 470$ and $\theta_E = 638$ may be used to compute the heat capacity of NiO and compared with observed values. Between 68 and 103°K., $C_p - C_v$ is estimated to be about 0.04 cal./mole(deg.). The exact value of this difference is unimportant, since it is used only in adjusting θ_D and θ_E to conform with low temperature C_p 's in order that the entropy at

68° may be estimated. The following is a comparison of computed values with experimental heat capacities:

| Temperature, °K. | C_D | C_E | C_v | C_p | $C_p(\text{comp}) - C_p(\text{obs.})$ |
|---------------------|-------|-------|-------|-------|---------------------------------------|
| 68 05 | 1.176 | 0.044 | 1.22 | 1 26 | -0.35 |
| 78 19 | 1.583 | 0.113 | 1.70 | 1.74 | -0.45 |
| 85 89 | 1.90 | 0.190 | 2.09 | 2.13 | -0.50 |
| 94.42 | 2.214 | 0.318 | 2.53 | 2 57 | -0.52 |
| 103.13 | 2.55 | 0.497 | 3 05 | 3.09 | -0.60 |

It will be noticed that the computed heat capacities are considerably smaller than the observed values and that both θ_D and θ_E should be decreased in order to raise the computed values. Since the Debye contribution is larger than the Einstein contribution, the next approximation may be attempted by adjusting θ_D at 68° to give the observed value of C_v without changing θ_E ; therefore

$$1.567 = 3RD \left(\frac{\theta_D}{T} \right) + 0.044;$$

and from Table D-1, $\theta_D/T = 6.10$ or $\theta_D = 415$. At 103°, this gives a computed C_p equal to 3.48, which is 0.21 cal. too small. The value of θ_E may now be decreased in order to make the computed value agree with the experimental value. This gives $\theta_E = 582$. With these two values, the heat capacities at 68 and 103°K. are then computed to be 1.65 and 3.69 cal., respectively. These two values for the characteristic functions may now be employed to estimate S_{68} .

It may be shown^{23,p.373} that the Debye contribution to the entropy is given by the relation

$$S_D = \frac{(C_v)_D}{3} + S_E',$$

where S_E' is the Einstein contribution to the entropy corresponding to the numerical value of θ_D . Furthermore, the Einstein contribution to the entropy equals the entropy of an harmonic oscillator of three degrees of freedom [Eq. (7.57)], which may be obtained from Tables E-2 and E-3. Accordingly, at 68°K.,

$$S_D = \frac{1.53}{3} + 0.082 + 0.011 = 0.603,$$

$$S_E = 0.0097 + 0.000 = 0.0097,$$

or the total entropy at 68°K. at constant volume equals 0.613 unit. The entropy at constant pressure is estimated to be 0.02 unit greater than this value; consequently

$$S_{68} = 0.633 \text{ cal./deg.}$$

The entropy between 68 and 298.1°K. may be determined by plotting $C_p/T - T$ or $C_p - \ln T$ and measuring the area under either curve between these two temperatures. Although the

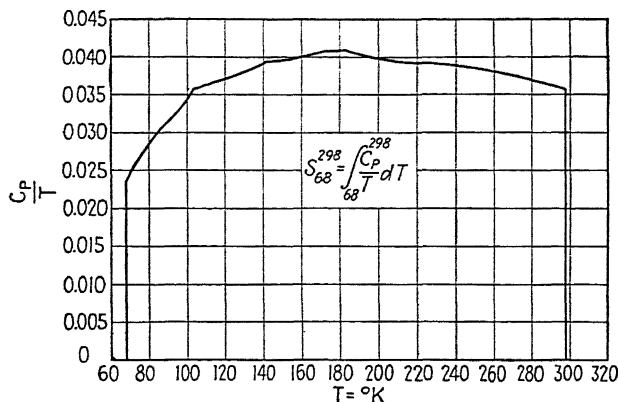


FIG. 8.—Plot for computing the third-law entropy of nickel oxide at 298.1°K.

second type of plot is apt to be somewhat simpler for graphical integration, the above data have been used to construct the $C_p/T - T$ plot presented in Fig. 8. The measured area under this curve between 68 and 298.1°K. corresponds to 8.58 entropy units; therefore

$$S_{298.1}(\text{NiO}) = 0.633 + 8.58 = 9.21 \text{ cal./ (mole) (deg.)}.$$

10. Evaluation of Entropy from Residual-ray Data.—At one time it was thought that the frequency of the so-called “residual rays” or Reststrahlen (observed when infrared radiation experiences practically metallic reflection at the surfaces of many crystalline substances) corresponded to the characteristic Einstein frequency of that substance. In fact, when the entropies of the metal halides are computed by using these characteristic

residual rays in conjunction with the Born and Von Kármán theory, excellent agreement between computed and calorimetric entropies is obtained. In such cases it appears that the agreement between the Einstein frequency and the residual-ray frequency is accidental and not generally true. The method of using residual-ray data is demonstrated by the following problem:

Illustration 5.—The observed residual-ray frequency for NaCl corresponds to 194 cm^{-1} .

Calculate the entropy of $\text{NaCl}_{(c)}$ at 298.1°K . and compare with the calorimetric value of $S_{298.1} = 17.3$ units.

Solution.—The frequency, $\omega = 194\text{ cm}^{-1}$, corresponds to a value of $\theta_E = 278$, and therefore $x_E = 0.934$ at 298.1°K . According to Rodebush,²⁴ $\theta_E = 1.35\theta_D$, and hence $\theta_D = 206$. The entropy at constant volume is, therefore,

$$S_{298} = S\left(\frac{\theta_D}{T}\right) + S\left(\frac{\theta_E}{T}\right) = S_D(0.692) + S_E(0.934).$$

From the table of Debye functions $(C_v)_D = 5.823$.

As pointed out in illustration 4,

$$S_D = \frac{(C_v)_D}{3} + S_E',$$

where S_E' is the Einstein contribution to the entropy corresponding to θ_D ; consequently $S_E' = 4.125 + 4.133$ and $S_D = 10.20$. From the table of Einstein functions $S_E = 3.603 + 2.98 = 6.58$ units.

In this example the vibration corresponding to each characteristic function is given three degrees of freedom. To convert this value of S_v to constant pressure, the empirical relation $S_p - S_v = \frac{2}{3}(C_p - C_v)$ is used (L-R, p. 150). Since $C_p - C_v$ is about $0.2\text{ cal./}(\text{deg.})(\text{g. atom})$, the difference $S_p - S_v$ equals 0.27 unit; therefore the computed entropy is

$$S_{298.1} = 10.20 + 6.58 + 0.27 = 17.05\text{ cal./deg.}$$

The preceding discussion illustrates the method of applying the Debye and Einstein theories of specific heats to atomic lattices. The procedure in the case of molecular lattices is somewhat different but equally important, since the crystal lattice of most organic compounds is of the molecular type. The essential difference between the two cases resides in the fact

that, whereas the atomic lattices contain point masses which can only undergo translational displacements equivalent to compressional waves, the molecular lattices are made up of molecules that possess three moments of inertia (two for diatomic or linear molecules). Consequently, the lattice motions consist of restricted translational motion of the center of gravity of the molecule, plus restricted (in general) rotation about the center of gravity. Thus molecular lattices absorb heat energy by reason of the compressional wave associated with translational vibrations plus a torsional wave associated with restricted rotations. On this basis the heat capacity of molecular lattices should require two Debye terms in order to take care of these two different types of wave motions. The case of free rotation is taken care of by assigning the equipartition value, $R/2$, corresponding to each moment of inertia of the molecule, to the heat capacity.

In addition to the thermal energy absorbed by these two waves, the internal vibrations of the molecule also absorb energy, since the molecule preserves its identity in the lattice. In the absence of such effects as hydrogen bonding these frequencies would be expected to be quite close to the fundamentals derived from infrared and Raman studies on the gaseous molecule; therefore, the contribution of these internal vibrations is readily computed by the methods described in Sec. 5. The molar-heat capacity at constant volume for such a crystal is, therefore,

$$C_v = 3RD(x_c) + 3RD(x_T) + \sum_{i=1}^n RE(x_i), \quad (7.71)$$

where $x_c = h\nu_D/kT$ for the compressional wave and x_T is the corresponding quantity for the torsional wave. The last term on the right-hand side represents the contribution to the heat capacity of the n internal, vibrational degrees of freedom of the molecule, treated as harmonic oscillators. If the molecule is diatomic or linear, the torsional Debye term becomes $2RD(x_T)$. Values of C_v computed by means of this equation may be converted to C_p by means of the standard thermodynamic relation

$$C_p - C_v = \frac{\alpha^2 VT}{\beta}, \quad (7.72)$$

where α is the coefficient of thermal expansion, β the coefficient of compressibility, and V the molar volume of the crystal.

11. Calculation of Heat Capacity of Molecular Lattices.

Illustration 6.—The heat capacity C_p of benzene at 15°K. , as given by Lord, Ahlberg, and Andrews,²⁵ equals 0.920 cal./mole. Lord and Andrews²⁶ give the following values for the 30 fundamental vibration frequencies of benzene (degeneracies in parentheses):

| cm. ⁻¹ | cm. ⁻¹ |
|-------------------|-------------------|
| 992.6(1) | 3063(1) |
| 3061.5(1) | 1854(1) |
| 606.4(2) | 1145(1) |
| 3048.3(2) | 538(1) |
| 1595(2) | 1520(1) |
| 1176(2) | 406(2) |
| 850(2) | 1025(2) |
| 670(1) | 1477(2) |
| 1190(1) | 3077(2) |
| 1008(1) | 1160(2) |

Compute the molar-heat capacity at constant pressure of crystalline benzene at 270°K.

Solution.—At low temperatures, such as 15°K. , the right-hand side of Eq. (7.72) is very small and hence $C_p \simeq C_v$. Consequently, from Eq. (7.71),

$$0.920 = 3RD \left(\frac{\theta_e}{15} \right) + 3RD \left(\frac{\theta_T}{15} \right) + \sum_1^{30} RE(x_i). \quad (7.73)$$

Since the lowest vibrational frequencies make the largest contribution to the internal heat capacity of the benzene molecule, the doubly degenerate vibration at 406 sets an upper limit to the individual contributions of the different frequencies to the observed heat capacity at 15°K. θ_e corresponding to 406 is 581; therefore x equals 38.8. Referring to Table E-1, it will be noticed that values of x greater than 13.9 contribute less than 0.0004 cal./deg. for a single degree of freedom; consequently, at 15°K. , the contribution of the internal benzene vibrations to the observed heat capacity is zero. Thus the observed value of 0.920 cal. equals the heat capacity contributed by the two Debye terms.

Assuming that the contribution of the two waves may be represented by an average value of θ_D ,

$$0.920 = 6RD \left(\frac{\theta_D}{T} \right)$$

or

$$3RD \left(\frac{\theta_D}{15} \right) = \frac{0.920}{2} = 0.460.$$

Referring to Table D-1, the value of T/θ_D corresponding to 0.460 is very nearly 0.100; consequently $\theta_D = 15/0.10 = 150$. The heat capacity of crystalline benzene at constant volume at any temperature is, therefore,

$$C_v = 6RD \left(\frac{150}{T} \right) + \sum_1^{30} RE \left(\frac{\theta_E}{T} \right), \quad (7.74)$$

and the value at constant pressure may be computed from Eq. (7.72). Lord, Ahlberg, and Andrews replace $(\alpha^2 V)/\beta$ in Eq. (7.72) by kC_v^2 , where $k = 6.45 \times 10^{-5}$ cal. $^{-1}$ for crystalline benzene; therefore

$$C_p = C_v + 6.45 \times 10^{-5} C_v^2 T. \quad (7.75)$$

In order to reduce the labor of computing the internal vibrational heat capacity of benzene, the frequencies will be lumped as follows:

| Frequency, cm. $^{-1}$ | Degeneracy | C_i |
|------------------------|------------|-------------------------------|
| 3062.5 | 6 | 0 |
| 1854 | 1 | 0.0099 |
| 1595 | 2 | 0.0594 |
| 1491 | 3 | 0.136 |
| 1118 | 9 | 1.680 |
| 992.6 | 1 | 0.287 |
| 850 | 2 | 0.908 |
| 670 | 1 | 0.760 |
| 606.4 | 2 | 1.788 |
| 538 | 1 | 1.049 |
| 406 | 2 | 2.740 |
| | | $\sum_1^{30} RE(x_i) = 9.417$ |

The total internal vibrational heat capacity at 270°K. is, therefore, 9.417 cal./(mole)(deg.). The Debye contribution, at 270°K., corresponding to $T/\theta_D = 1.800$ (as read from Table D-1), is twice 5.87; that is, $6RD(150/270) = 11.74$ cal.

Consequently,

$$C_v = 6RD(150/270) + \sum_1^{30} RE(x_i) = 11.74 + 9.42 \\ = 21.16 \text{ cal./}(\text{mole})(\text{deg}).$$

The molar-heat capacity at constant pressure and 270°K. is then computed from Eq. (7.75):

$$C_p = 21.16 + 6.45 \times 10^{-5}(21.16)^2(270) = 21.16 + 7.80 \\ = 28.96 \text{ cal./}(\text{mole})(\text{deg}).$$

The observed heat capacity at this temperature is 29.7 cal. corresponding to a discrepancy of 2.5 per cent in the calculated value.

Lord, Ahlberg, and Andrews have carefully computed the heat capacity of benzene at 10° intervals between 4 and 270°K. by the foregoing procedure; except for the values at 25 and 270°K., the discrepancies between computed and observed heat capacities are less than 1 per cent.

12. Heats of Dissociation from Spectroscopic Data.—The absorption spectra of many molecules exhibit regions of line or discrete absorption, in which the spacing of successive vibrational bands decreases with increasing frequency; eventually the spectra go over into regions of continuous absorption, characterized by the complete absence of fine structure. The decreased spacing of the vibrational levels with increasing frequency is due to the fact that the normal modes of vibration are not strictly equivalent to harmonic oscillators but are actually anharmonic; the energy levels, instead of being expressed by Eq. (7.52), are expressed by the equation

$$E_v = (v + \frac{1}{2})h\nu - (v + \frac{1}{2})^2xh\nu, \quad (7.76)$$

where v is the vibrational quantum number (0, 1, 2, . . .). The constant x measures the deviation from harmonic behavior and is called the “anharmonicity coefficient.” Obviously, the spacing of successive vibrational lines will decrease if this relation is true.

The explanation of the cessation of discrete absorption followed by continuous absorption is that, as the molecule attains

higher and higher vibrational levels, the frequency of oscillational motion increases to the point where the vibrating parts can no longer stay together and the molecule decomposes. Thus the molecule possessing quantized energy levels ceases to exist as such, and the absorption becomes continuous. If the molecule is diatomic, the products of dissociation must be two atoms; if the molecule is polyatomic, the products of dissociation will usually contain more complex fragments. Thus, only in the case of diatomic molecules are the products of photodissociation fairly definite; even in this case uncertainties may exist regarding the state of excitation of the products. Since the calorimetric heats of formation employed in thermochemical calculations refer to the ground state of all species concerned, it is important that heats of dissociation of diatomic molecules, deduced from spectroscopic data, be adjusted to this basis from known energy level data or else not be employed in ordinary thermochemical considerations. For example, the wave length at which discrete absorption ends and the continuous begins (convergence limit) in the chlorine spectrum is $4,785\text{\AA}$ ($2.09 \times 10^4 \text{ cm.}^{-1}$), which is equivalent to $59,400 \text{ cal./mole}$. However, this figure cannot be used as the heat of formation of 2Cl from Cl_2 unless auxiliary spectroscopic data are available or the calorimetric heat of dissociation is known, because this datum alone does not prove that two normal chlorine atoms are produced by photodissociation. Another method for determining the heat of dissociation, which does not depend on the observation of the convergence limit, is that due to Birge and Sponer.²⁷ This method is based on the fact that, since the convergence limit is the state of maximum vibrational energy for the molecule before it dissociates, the corresponding vibrational quantum number at convergence is determined by differentiation of Eq. (7.76) with respect to v and equating to zero:

$$\frac{dE_v}{dv} = h\nu - 2(v_c + \frac{1}{2})xh\nu = 0. \quad (7.77)$$

In this equation, v_c is the vibrational quantum number at the convergence limit. Therefore

$$v_c = \frac{1}{2x} - \frac{1}{2}; \quad (7.78)$$

substituting this value for v_c in Eq. (7.76) gives

$$E_c = \frac{h\nu}{4x} \quad (7.79)$$

for the total vibrational energy at the convergence limit. The energy in excess of the zero-point vibrational energy is

$$E_c' = \frac{h\nu}{4x} - \frac{h\nu}{2} \quad (7.80)$$

if the small $xh\nu/4$ term is neglected. This, then, represents the energy required to dissociate a diatomic molecule into atoms at the absolute zero, since no cognizance is taken of any possible contribution from the kinetic energy of the molecule before dissociation, or kinetic energy given to the atoms after dissociation.

In some cases the quantum of radiation absorbed is sufficient to raise the molecule to a vibrational level of an upper electronic state such that dissociation can take place. In this case, if the height of the zero vibrational level of the upper state above the zero of the ground state is known, the dissociation energy for the upper level can be computed; but it is of no great significance for ordinary thermochemical calculations.

13. The Heat of Dissociation of Chlorine. *Illustration 7.*—The vibrational energy levels of the $\text{Cl}_{35}\text{Cl}_{35}$ molecule (in reciprocal centimeters) are given by the equation^{20, p. 309}

$$\omega_{35} = 564.1(v + \frac{1}{2}) - 3.99(v + \frac{1}{2})^2,$$

and for the $\text{Cl}_{35}\text{Cl}_{37}$

$$\omega_{37} = 556.1(v + \frac{1}{2}) - 3.89(v + \frac{1}{2})^2.$$

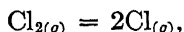
The moment of inertia^{20, p. 314} of Cl_2 equals 114×10^{-40} g. cm.²

Chlorine atoms possess the following energy levels:

| Term | Energy, cal./mole | Weight, $-p$ |
|-------------|-------------------|--------------|
| $^2P_{3/2}$ | Ground | 4 |
| $^2P_{1/2}$ | 2,505 | 2 |

a. Compute the energy of dissociation of Cl_2 at 0°K .

b. Compute the ΔH for the reaction



at 25°C .

c. Explain the discrepancy between the result of (b) and the value 59,400 cal. computed from the convergence limit at 4,785Å. What is the heat of formation of $\text{Cl}_{(g)}$ at 25°C.?

Solution.—a. The anharmonicity coefficients for the two chlorine molecules are

$$x_{35} = \frac{3.99}{564.1} = 7.07 \times 10^{-3} \quad x_{37} = \frac{3.89}{556.1} = 7.00 \times 10^{-3}.$$

From Eq. (7.80), the heat of dissociation of $\text{Cl}_{35}\text{Cl}_{35}$ in calories is

$$D_{35} = \frac{(564.1)(2.844)}{4(7.07)10^{-3}} - \frac{(2.844)(564.1)}{2} = 55,900 \text{ cal./mole};$$

for the $\text{Cl}_{35}\text{Cl}_{37}$

$$D_{37} = \frac{(556.1)(2.844)}{4(7.00)10^{-3}} - \frac{(2.844)(556.1)}{2} = 55,710 \text{ cal./mole}.$$

The dissociation energy for the naturally occurring isotopic mixture consisting of 60 per cent $\text{Cl}_{35}\text{Cl}_{35}$ and 40 per cent $\text{Cl}_{35}\text{Cl}_{37}$ would, therefore, be

$$D = (0.6)(55,900) + (0.4)(55,710) = 55,820 \text{ cal./mole}.$$

The value of the dissociation energy obtained by this procedure corresponds to the reaction at the absolute zero.

$$\text{Cl}_{2(g)} = 2\text{Cl}_{(g)} \quad \Delta E_0^\circ = 55,820.$$

b. The heat of this reaction at 25°C. may then be computed from the relation

$$\Delta H_{298} = 55,820 + 2(H_{298}^\circ - E_0^\circ)_{\text{Cl}} - (H_{298}^\circ - E_0^\circ)_{\text{Cl}_2}. \quad (7.81)$$

This may be done as follows: From the relation

$$H^\circ = E^\circ + PV = E_0^\circ + RT^2 \frac{d \ln Q}{dT} + \frac{5}{2} RT, \quad (7.82)$$

where $RT^2 \frac{d \ln Q}{dT} = \frac{N \sum \epsilon p e^{-\epsilon/kT}}{Q}$ [see Eq. (7.14)], the heat contents of Cl_2 and 2Cl at 298.1°K. may be evaluated with respect to the absolute zero.

For Cl.—The partition function for Cl atoms may be computed from the foregoing energy levels.

$$Q_{\text{Cl}}^{298} = 4 + 2e^{-2,505/592.3} = 4 + 2e^{-4.23} = 4 + 2(0.0146) = 4.029.$$

Consequently

$$RT^2 \frac{d \ln Q}{dT} = \frac{(2,505)(2)(0.0146)}{4.029} = 18.18;$$

substituting in Eq. (7.82) gives

$$2(H^\circ - E_0^\circ) = 2(18.18 + \frac{5}{2}RT) = 2(1,499) = 2,998 \text{ cal.}$$

For Cl_2 .—The average fundamental frequency for the natural isotopic mixture of chlorine molecules may be taken from the foregoing equations as 561 cm.^{-1} . The approximate partition function is

$$Q = Q_R \cdot Q_v$$

where

$$Q_R = \frac{8\pi^2 I k T}{s h^2} \quad (s = 2)$$

$$Q_v = (1 - e^{-h\nu/kT})^{-1}.$$

$$\ln Q_R \cdot Q_v = \ln Q_R + \ln Q_v$$

Therefore

$$\begin{aligned} RT^2 \frac{d \ln Q_R \cdot Q_v}{dT} &= RT^2 \left(\frac{d \ln Q_R}{dT} + \frac{d \ln Q_v}{dT} \right) \\ &= RT + RT \frac{x}{e^x - 1} = RT \left(1 + \frac{x}{e^x - 1} \right), \end{aligned}$$

where $x = \frac{h\nu}{kT} = \frac{804}{298.1} = 2.70$. Therefore, $\frac{x}{e^x - 1} = 0.194$ and

$$RT^2 \frac{d \ln Q}{dT} = 592.3(1.194) = 709.$$

The heat content of $\text{Cl}_{2(g)}$ in excess of the zero-point energy at 298.1° is, therefore,

$$(H^\circ - E_0^\circ) = 709 + 2.5(592.3) = 709 + 1,481 = 2,190 \text{ cal.}$$

Substituting the above heat-content data for 2Cl and Cl_2 in Eq. (7.81) gives

$$\Delta H_{298} = 55,820 + 2,998 - 2,190 = 56,630 \text{ cal./mole.}$$

c. As just pointed out, the heat of dissociation of Cl_2 , as determined by the convergence limit at $4,785\text{\AA}$, which is equivalent to $59,400 \text{ cal.}$, does not necessarily correspond to dissociation into two normal Cl atoms. If it is assumed that the dissociation effected by radiation of this frequency corresponds to the production of one normal Cl atom and one Cl atom in the $^2P_{1/2}$ state,

then the energy for the dissociation into two normal atoms would be $59,400 - 2,500 = 56,900$ at 0°K . This figure is in fair agreement with the indirectly computed value (55,820), which makes it very probable that the photodissociation produces one normal and one excited Cl atom. The value 56,900 should be used in thermochemical calculations after correction to 25°C . by the procedure given in (b). Consequently, for the process



The standard heat of formation of $\text{Cl}_{(g)}$ is then 28,854 cal./mole at 25°C .

14. The Third Law of Thermodynamics.—In Chap. VI, Sec. 1, the statement of the third law favored by Eastman and Milner²⁸ was given with the admission that further elaboration was required. This may be advantageously undertaken by considering some of the apparent contradictions to this law in the light of the foregoing discussion of the statistical computation of entropies. When the entropies of gaseous N_2O , NO , CO , and H_2O are computed from spectroscopic data and compared with the calorimetric values, the following results are obtained:

MOLAR ENTROPIES AT 298.1°K .

| | Spectroscopic | Calorimetric | Δ |
|--|---------------|--------------|----------|
| N_2O | 52.581 | 51.44 | 1.14 |
| NO (121.4°K .) | 43.75 | 43.0 | 0.75 |
| CO | 47.316 | 46.2 | 1.12 |
| H_2O | 45.17 | 44.23 | 0.94 |

It will be noted that the spectroscopic entropy is greater than the calorimetric value, by amounts ranging from 0.75 to 1.14 units, for all four molecules.

In accordance with the quantum theory, a system containing a mole of identical particles, when cooled at a slow enough rate to permit attainment of equilibrium all the way down, will eventually drop into the lowest energy level at the absolute zero. If the system can exist in only one configuration or state under these conditions, the entropy is zero, in accordance with the Planck relation,

$$S = R \ln g, \quad (7.83)$$

since the multiplicity g then equals unity. If now, in the case of N_2O , NO , and CO , it is impossible, because of the similarity of the sizes of the atoms on both ends of the molecule, for the molecules to distinguish between orientations of the type $\text{NO}-\text{NO}$ or $\text{NO}-\text{ON}$ in the crystal, and if these two states possess practically identical energy, the degeneracy or multiplicity of the lowest level is two; hence the entropy at the absolute zero would be

$$S_0 = R \ln 2 = 1.38 \text{ units.}$$

The fact that the discrepancy is never quite 1.38 is explained by some tendency towards ordering, owing to one orientation's being preferred to the other.

In these cases the calorimetric entropy is smaller than the spectroscopic, because, as the temperature is lowered, the rate at which the system passes over to the ordered arrangement required by the third law is very slow compared to the time required for observations; hence the observed heat capacities at very low temperatures are smaller than they would be if true equilibrium were attained. Consequently the area under the $C_p - \ln T$ curve used to evaluate the entropy is too small and the spectroscopic value is the more accurate value. The discrepancy between the statistical and the calorimetric entropy of H_2O is believed to be connected with the coordination of the water molecules through hydrogen bonds in the crystal.

Another source of discrepancies between calorimetric and spectroscopic entropies is the establishment of false equilibria between ortho and para forms of molecules (H_2 , D_2 , etc.) possessing nuclear spins. Ordinary hydrogen consists of three moles of ortho hydrogen to 1 mole of para at temperatures above room temperature, but with decreasing temperature the proportion of para increases. At the absolute zero, all the hydrogen should be in the 0th rotational level of the para form, if true equilibrium is attained. Actually, unless activated charcoal or ammonia synthesis catalyst is in contact with the hydrogen, the rate at which ortho goes over to para is so slow that during the usual course of measuring the heat capacity, the high temperature ratio of ortho to para is maintained. Instead of the entropy of this mixture falling to zero at the absolute zero, it is greater by the sum of the degeneracy of the lowest rotational state (9) of ortho hydrogen, plus the entropy of mixing due to the fact that

the crystal is a solid solution of 1 part para H_2 plus 3 parts ortho H_2 . Thus 4.39 units must be added to the entropy deduced from the $C_p - \ln T$ plot in order to obtain the entropy of the actual mixture of 3:1 hydrogen used in the calorimetric experiments. Here again, it should be noted that if true equilibrium were attained at the absolute zero, all the H_2 would be para and the entropy would be zero, *i.e.*, there would be no multiplicity or mixing entropy.

The entropies of glasses, which are crystals not in a state of equilibrium, have been the subject of a number of careful investigations. In all cases it was found that glasses possess a positive entropy at the absolute zero which is believed to be due to the existence of several states of the molecule of practically identical energy, which differ slightly in orientation or relative position of the molecules. This entropy will doubtless vanish if the glasses are maintained at very low temperatures long enough for the glass to come to equilibrium.

The assignment of zero entropy to molecules known to consist of mixtures of isotopes, instead of allotting a residual entropy of

$$S_M = -R \sum N_i \ln N_i \quad (7.84)$$

at the absolute zero, is justifiable. Eastman²⁹ has pointed out that the proportions of the mixtures do not change significantly in chemical reactions and, therefore, this term need not be included in the evaluation of the practical entropies used in thermochemistry. It is hoped that the foregoing sketchy discussion has clarified the statement of the third law, given in Chap. VI, to some extent. The reader is referred to the chapter on Statistical Methods in Glasstone's "Recent Advances in General Chemistry"³⁰ for further expansion and clarification of some of the theoretical discussions presented in this chapter.

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CHAPTER VIII

SPECIAL METHODS (SEMIEMPIRICAL)

The present chapter deals with methods for estimating entropies, free energies, and heat capacities by various empirical and semiempirical procedures. In view of the structural regularities in organic compounds, it is not surprising that the most extensive and reliable methods are available for these compounds; whereas the procedures available for inorganic compounds are limited in scope and reliability. Regardless of which class of compounds is under consideration, the most generally useful method for estimating free energies is the indirect method of estimating entropies, in conjunction with the known values for heats of formation. Furthermore, it is very often possible to make good guesses for entropies, simply by analogy or a common-sense study of all known entropy data for either class of compounds. The significance of this statement will become clearer as the presentation of the data develops.

1. The Method of Structural Similarity.—The rules for estimating entropies and free energies of organic compounds, based on observed regularities in homologous series and the effect of certain definite structural modifications on these two items, have been summarized by Parks and Huffman in their monograph.¹ On the basis of some newer data, Parks² has made a review of the entropy and free-energy relations among the paraffin and olefin hydrocarbons. The available data on the entropy of the normal paraffins in the gaseous state indicate that the entropy of this series of compounds may be satisfactorily expressed by means of the equation

$$S_{298} = 34.0 + 10.0n, \quad (8.1)$$

where n is the number of carbon atoms in the molecule and 10 represents the entropy increment per CH_2 group. The increment in the standard molar free energies of formation of this series of compounds is plus 1,440 cal. per CH_2 group, that is, the higher members of the series become increasingly less stable. The

effect of branching in the paraffin series is, in general—but not always—to produce an isomer which is more stable than the normal compound.

In the case of olefinic compounds, the entropy is usually less than the entropy of the corresponding paraffin by about 2.4 units, regardless of state. The effect on the molar free energy of formation is that the olefin is about 20,000 cal. less stable than the corresponding paraffin. Similar regularities are observed in the entropies and free energies of formation of normal aliphatic alcohols. A more extensive discussion of the subject will be found in the chapter on the effect of modifications in molecular structure upon the molar entropy and free energy, in the monograph by Parks and Huffman. These rules have proved to be an invaluable aid in discussing the thermodynamics of organic compounds.

2. Estimation of Entropies of Organic Compounds.—Strelkoff³ presents a tabulation of the entropies of organic compounds, which are in either the solid or the liquid state at room temperature. A study of the relation between the molar heat capacities at constant pressure and the entropies at 298°K. has led Strelkoff to formulate the following approximate rules for computing the entropies of organic compounds when C_p is known at room temperature:

$$S_{298} = 1.1C_p. \quad (\text{Solids}) \quad (8.2)$$

$$S_{298} = 1.4C_p. \quad (\text{Liquids}) \quad (8.3)$$

The molar heat capacities and entropies at 25°C. are given for a few of the compounds cited by Strelkoff in Table 1.

Since it is very often the case that the entropies of structurally similar organic compounds in the solid or liquid state are not spread over much of a range, it is possible to make rough, workable estimates of entropies when the entropy of some related compounds is known. For example, the entropy of solid benzoic acid at 25°C. equals 40.8 units and, as a first approximation, it might be guessed that the entropy of solid benzene sulphonic acid would be about 45 units. That is, a moderate increase has been allowed for the replacement of the CO group by the more complex SO₂ group. Again, the entropies of liquid nitrobenzene, benzyl alcohol, and aniline at 25°C. are 53.6, 51.8, and 45.8 units, respectively. Since the molecular weight of

benzaldehyde is closest to benzyl alcohol but contains one molecule of H_2 less, a value of about 49 units should be a fair approximation to the entropy of this compound. On the other hand, it should not be concluded that the entropies of *n*-butyl alcohol and diethyl ether are equal because they are isomeric compounds. The entropies of these two liquids are 54.5 and 60.5 units, respectively—a difference due to the structural dissimilarity of the two compounds.

TABLE 1.—THE RELATION BETWEEN HEAT CAPACITY AND ENTROPY AT 25°C. FOR SOME ORGANIC COMPOUNDS

| Compound | Melting point, °K. | Boiling point, °K. | C_P | S | $\frac{S}{C_P}$ |
|----------------------|--------------------|--------------------|-------|------|-----------------|
| Anthracene..... | 490 | 624 | 49.5 | 49.6 | 1.003 |
| Stilbene..... | 397 | 580 | 54.2 | 60.0 | 1.108 |
| Phenol..... | 314 | 454 | 31.8 | 34.0 | 1.070 |
| Benzoic acid..... | 394 | 522 | 34.7 | 40.8 | 1.175 |
| Urea..... | 406 | | 22.4 | 25.2 | 1.123 |
| 2-Methyl butane..... | 115 | 303 | 37.5 | 60.8 | 1.621 |
| Benzene..... | 278.5 | 353 | 32.1 | 41.9 | 1.304 |
| Ethylene glycol..... | 261.5 | 470.5 | 35.7 | 39.9 | 1.118 |
| CCl_4 | 251 | 349.7 | 31.7 | 49.1 | 1.547 |
| Dioxane..... | 284.1 | 373 | 34.9 | 47.0 | 1.348 |

The replacement of the two hydroxyl groups of ethylene glycol ($S_{298} = 39.9$) by chlorine atoms produces the compound, ethylene dichloride, having an entropy equal to 49.84 units. Thus the effect of replacing an OH group of a polyhydric alcohol by a Cl atom is an average entropy increase of 5.0 units in the liquid state. It might therefore be estimated that the entropy of glyceryl trichlorohydrin would be about 15 units greater than glycerin (48.87), or about 64 cal./(mole)(deg.). Similarly, the entropy of liquid glycolchlorohydrin would be about 45.0 units at 25°C. The corresponding free energies may readily be estimated when the necessary data on heats of combustion or formation are available.

The foregoing examples are illustrative of the sort of considerations that may be employed to evaluate rough, preliminary values for entropies and free energies of compounds that have not been subjected to thermodynamic studies. In order to facilitate the

(Text continues on p. 175.)

TABLE 2.—THE MOLAR ENTROPY OF SOME SOLID AROMATIC COMPOUNDS AT 25°C.


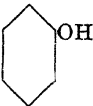
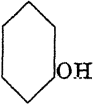


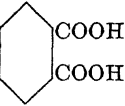
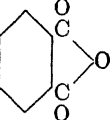
| Compound | Formula | Entropy |
|---|---|-------------------|
| Phenol. | OH  | 34.0 |
| Catechol. | OH  | 35.9 |
| Resorcinol. | OH  | 35.3 |
| Hydroquinone. | OH  | 33.5 |
| <i>p</i> -Dichlorobenzene. | C ₆ H ₄ Cl ₂ | 41.9 |
| 1,2,4,5-Tetrachlorobenzene. | C ₆ H ₂ Cl ₄ | 55.2 |
| Hexachlorobenzene. | C ₆ Cl ₆ | 71.2 |
| <i>p</i> -Dibromobenzene. | C ₆ H ₄ Br ₂ | 46.4 |
| Benzoic acid. | COOH  | 40.8 |
| <i>o</i> -Hydroxy benzoic acid. | C ₆ H ₄ (OH)COOH | 42.6 |
| <i>m</i> -Hydroxy benzoic acid. | C ₆ H ₄ (OH)COOH | 42.3 |
| <i>p</i> -Hydroxy-benzoic acid. | C ₆ H ₄ (OH)COOH | 42.0 |
| Phthalic acid. | COOH  | 49.7 ⁴ |
| Phthalic anhydride. |  | 42.9 ⁴ |

TABLE 2.—THE MOLAR ENTROPY OF SOME SOLID AROMATIC COMPOUNDS AT 25°C.—(Continued)

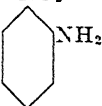
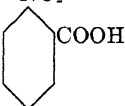
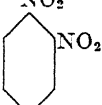
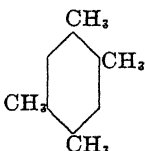

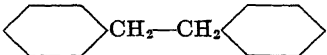
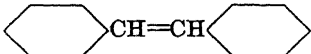
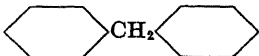
| Compound | Formula | Entropy |
|----------------------------------|--|---------|
| <i>o</i> -Nitroaniline..... | NO_2  | 42.1 |
| <i>m</i> -Nitroaniline..... | $\text{C}_6\text{H}_4(\text{NO}_2)(\text{NH}_2)$ | 42.1 |
| <i>p</i> -Nitroaniline..... | $\text{C}_6\text{H}_4(\text{NO}_2)(\text{NH}_2)$ | 42.1 |
| <i>o</i> -Nitrobenzoic acid..... | NO_2  | 49.8 |
| <i>m</i> -Nitrobenzoic acid..... | $\text{C}_6\text{H}_4(\text{NO}_2)(\text{COOH})$ | 49.0 |
| <i>p</i> -Nitrobenzoic acid..... | $\text{C}_6\text{H}_4(\text{NO}_2)(\text{COOH})$ | 50.2 |
| <i>o</i> -Dinitrobenzene..... | NO_2  | 51.7 |
| <i>m</i> -Dinitrobenzene..... | $\text{C}_6\text{H}_4(\text{NO}_2)_2$ | 52.8 |
| 1,2,4,5-Tetramethylbenzene .. |  | 58.7 |
| 1,2,3,4,5-Pentamethylbenzene.. | $\text{C}_6\text{H}(\text{CH}_3)_5$ | 70.3 |
| Hexamethylbenzene..... | $\text{C}_6(\text{CH}_3)_6$ | 74.0 |
| Diphenyl..... |  | 49.2 |
| Diphenylethane..... |  | 64.6 |
| Diphenylethylene (stilbene)... |  | 60.0 |
| Diphenylmethane..... |  | 57.2 |

TABLE 2.—THE MOLAR ENTROPY OF SOME SOLID AROMATIC COMPOUNDS AT 25°C.—(Continued)

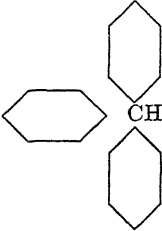
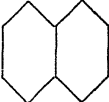
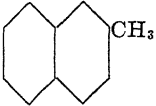
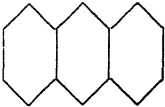
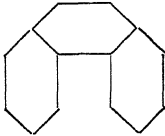
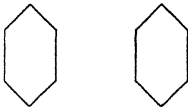
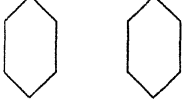
| Compound | Formula | Entropy |
|----------------------------------|---|---------|
| Triphenylmethane..... |  | 74.6 |
| Tetraphenylmethane.... | $C(C_6H_5)_4$ | 91.6 |
| Naphthalene..... |  | 39.9 |
| β -Methylnaphthalene. |  | 48.7 |
| Anthracene..... |  | 49.6 |
| Phenanthrene..... |  | 50.6 |
| Dibenzoylethylene..... | $COCH=CHCO$  | 76.3 |
| Dibenzoylthane..... | $COCH_2CH_2CO$  | 77.6 |

TABLE 2.—THE MOLAR ENTROPY OF SOME SOLID AROMATIC COMPOUNDS AT 25°C.—(Continued)

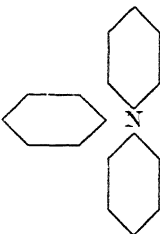
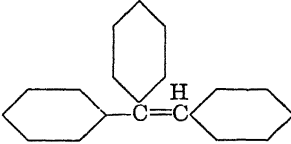
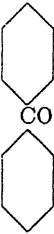
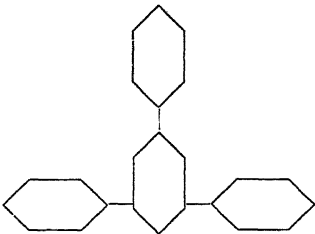

| Compound | Formula | Entropy |
|------------------------|---|-------------------|
| Triphenyl amine..... |  | 73.0 |
| Triphenylethylene..... |  | 78.7 |
| Benzophenone..... |  | 58.6 |
| Triphenyl benzene..... |  | 87.8 ⁴ |
| Diphenyl carbinol..... |  | 57.3 |

TABLE 2.—THE MOLAR ENTROPY OF SOME SOLID AROMATIC COMPOUNDS AT 25°C.—(Continued)

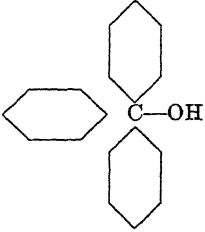
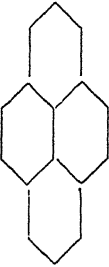
| Compound | Formula | Entropy |
|-------------------------|---|---------|
| Triphenyl carbinol..... |  | 78.7 |
| Pyrene..... |  | 51.4 |

TABLE 3.—THE MOLAR ENTROPY OF SOME LIQUID AROMATIC COMPOUNDS AT 25°C.



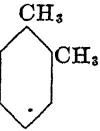
| Compound | Formula | Entropy |
|-----------------------|---|---------|
| Benzene..... |  | 41.9 |
| Toluene..... |  | 52.4 |
| <i>o</i> -Xylene..... |  | 59.3 |
| <i>m</i> -Xylene..... | $C_6H_4(CH_3)_2$ | 60.3 |
| <i>p</i> -Xylene..... | $C_6H_4(CH_3)_2$ | 60.5 |

TABLE 3.—THE MOLAR ENTROPY OF SOME LIQUID AROMATIC COMPOUNDS
AT 25°C.—(Continued)


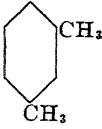
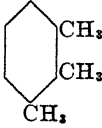
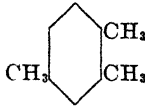



| Compound | Formula | Entropy |
|-----------------------------|---|---------|
| Ethyl benzene..... | C_2H_5  | 61.2 |
| Pseudocumene..... | CH_3  CH_3 | 67.7 |
| Prehnitene..... | CH_3  CH_3 | 69.5 |
| Isodurene..... | CH_3  CH_3 | 74.1 |
| <i>p</i> -Cymene..... | CH_3  C_2H_5 | 73.3 |
| <i>n</i> -Butylbenzene..... |  C_4H_9 | 76.8 |
| tert-Butylbenzene..... |  $C(CH_3)_3$ | 66.6 |

TABLE 3.—THE MOLAR ENTROPY OF SOME LIQUID AROMATIC COMPOUNDS
AT 25°C.—(Continued)


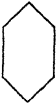




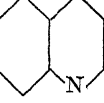
| Compound | Formula | Entropy |
|----------------------|---|-------------------|
| Nitrobenzene | NO ₂  | 53.6 ⁴ |
| Benzyl alcohol | CH ₂ OH  | 51.8 ⁴ |
| Fluorbenzene | C ₆ H ₅ F | 46.6 ⁵ |
| Chlorbenzene | C ₆ H ₅ Cl | 47.2 ⁵ |
| Brombenzene | C ₆ H ₅ Br | 49.7 ⁵ |
| Iodobenzene | C ₆ H ₅ I | 49.1 ⁵ |
| Thiophenol | SH  | 52.6 ⁴ |
| Aniline | NH ₂  | 45.8 |
| Thiophene |  | 42.2 |
| Pyridine | N  | 42.8 ⁴ |
| Quinoline |  | 51.9 ⁴ |

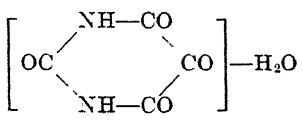
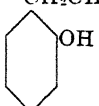
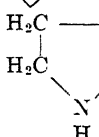
TABLE 4.—THE MOLAR ENTROPY OF SOME SOLID ALIPHATIC COMPOUNDS AT 25°C.

| Compound | Formula | Entropy |
|--------------------------------------|--|--------------------|
| Oxalic acid..... | $(\text{COOH})_2$ | 28.7 |
| Urea..... | $\text{CO}(\text{NH}_2)_2$ | 25.2 |
| Glycine..... | $\text{NH}_2\text{CH}_2\text{COOH}$ | 26.1 |
| Erythritol..... | $\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$ | 39.9 |
| Mannitol..... | $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$ | 57.0 |
| Dulcitol..... | $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$ | 56.0 |
| <i>d</i> , α -Glucose..... | $\text{C}_6\text{H}_{12}\text{O}_6$ | 50.7 |
| β -Lactose..... | $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ | 96.4 ⁶ |
| Sucrose..... | $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ | 86.1 |
| Fumaric acid..... | $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ | 39.7 |
| Maleic acid..... | $\text{HC}=\text{CH}-\text{COOH}$ | 38.1 |
| Succinic acid..... | $\text{H}_2\text{C}-\text{COOH}$ | 42.0 |
| Amyl amine hydrochloride..... | $\text{C}_5\text{H}_{11}\text{NH}_2\text{HCl}$ | 63.7 |
| Stearic acid..... | $\text{C}_{17}\text{H}_{35}\text{COOH}$ | 129.9 |
| Palmitic acid..... | $\text{C}_{15}\text{H}_{31}\text{COOH}$ | 113.7 |
| Hexamethylethane.. | $(\text{CH}_3)_3\text{C}\cdot\text{C}(\text{CH}_3)_3$ | 61.4 |
| Eicosane..... | $\text{C}_{20}\text{H}_{42}$ | 133.5 |
| Pentacosane..... | $\text{C}_{25}\text{H}_{52}$ | 160.4 |
| Trtriacontane..... | $\text{C}_{33}\text{H}_{68}$ | 209.8 |
| <i>dl</i> -Alanine..... | $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ | 31.6 |
| <i>d</i> (<i>l</i>)-Lactic acid... | $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ | 34.30 ⁷ |
| <i>l</i> (<i>d</i>)-Lactic acid... | $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ | 34.00 ⁷ |
| <i>l</i> -Asparagine..... | $\text{CH}_3\text{C}(\text{NH}_2)(\text{COOH})\text{CONH}_2$ | 41.7 |
| <i>l</i> -Asparagine hydrate | $\text{CH}_3\text{C}(\text{NH}_2)(\text{COOH})\text{CONH}_2\cdot\text{H}_2\text{O}$ | 51.0 |
| <i>l</i> -Aspartic acid..... | $\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ | 41.5 |
| <i>d</i> -Glutamic acid.... | $\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ | 45.7 |
| Glutamic acid hydrochloride..... | $\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}\cdot\text{HCl}$ | 59.33 ⁷ |
| Creatine..... | $\text{H}_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$ | 45.3 |
| Creatine hydrate... | $\text{H}_2\text{NC}(=\text{NH})\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}\cdot\text{H}_2\text{O}$ | 56.0 ⁸ |
| Creatinine..... | $\begin{array}{c} \text{NH}-\text{CO} \\ \\ \text{HN}=\text{C} \\ \\ \text{N}-\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ | 40.1 |

TABLE 4.—THE MOLAR ENTROPY OF SOME SOLID ALIPHATIC COMPOUNDS AT 25°C.—(Continued)

| Compound | Formula | Entropy |
|--|--|--------------------|
| <i>dl</i> -Leucine | $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ | 49.5 ⁹ |
| <i>dl</i> -Ornithine | $\text{H}_2\text{NCH}_2(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$ | 46.2 ⁸ |
| Ornithine dihydrochloride | $\text{H}_2\text{NCH}_2(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH} \cdot 2\text{HCl}$ | 70.25 ⁷ |
| <i>dl</i> -Citrulline | $\text{H}_2\text{NCONHCH}_2(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$ | 60.8 ⁸ |
| <i>d</i> -Arginine | $\text{H}_2\text{NC}(=\text{NH})\text{NHCH}_2(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH}$ | 59.9 ⁹ |
| Guanidine carbonate | $(\text{H}_2\text{NC}(=\text{NH})\text{NH}_2)_2 \cdot \text{H}_2\text{CO}_3$ | 70.59 ⁷ |
| Cysteine | $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$ | 40.6 |
| Cystine | $(-\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH})_2$ | 68.5 |
| β, β' -Dithiodilactic acid | $(-\text{SCH}_2\text{CH}_2\text{COOH})_2$ | 65.5 |
| Adenine | $\begin{array}{c} \text{N}=\text{C}-\text{NH}_2 \\ \\ \text{HC} \quad \text{C}-\text{N} \begin{array}{l} \text{H} \\ \diagup \end{array} \\ \quad \quad \diagdown \\ \text{N}=\text{C}-\text{N}=\text{CH} \\ \quad \\ \text{N}=\text{C}-\text{OH} \end{array}$ | 36.1 |
| Hypoxanthine | $\begin{array}{c} \text{HC} \quad \text{C}-\text{N} \begin{array}{l} \text{H} \\ \diagup \end{array} \\ \quad \quad \diagdown \\ \text{N}=\text{C}-\text{N}=\text{CH} \\ \quad \\ \text{N}=\text{C}-\text{OH} \end{array}$ | 34.8 |
| Guanine | $\begin{array}{c} \text{N}=\text{C}-\text{OH} \\ \quad \\ \text{H}_2\text{NC} \quad \text{C}-\text{N} \begin{array}{l} \text{H} \\ \diagup \end{array} \\ \quad \quad \diagdown \\ \text{N}=\text{C}-\text{N}=\text{CH} \\ \quad \\ \text{N}=\text{C}-\text{OH} \end{array}$ | 38.3 |
| Uric acid | $\begin{array}{c} \text{N}=\text{C}-\text{OH} \\ \quad \\ \text{HO}-\text{C} \quad \text{C}-\text{N} \begin{array}{l} \text{H} \\ \diagup \end{array} \\ \quad \quad \diagdown \\ \text{N}=\text{C}-\text{N}=\text{C}-\text{OH} \end{array}$ | 41.4 |
| Allantoin | $\begin{array}{c} \text{HN}-\text{CHNHCONH}_2 \\ \\ \text{O}=\text{C} \quad \\ \quad \\ \text{HN}-\text{C}=\text{O} \end{array}$ | 46.6 |

TABLE 4.—THE MOLAR ENTROPY OF SOME SOLID ALIPHATIC COMPOUNDS AT 25°C.—(Continued)

| Compound | Formula | Entropy |
|-------------------------------|---|-------------------|
| Alloxan |  | 44.6 |
| <i>l</i> -Tyrosine* | $\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$  | 53.0 ⁹ |
| <i>l</i> -Proline |  | 40.8 ⁸ |
| Taurine | $\text{H}_2\text{NCH}_2\text{CH}_2\text{SO}_3\text{H}$ | 36.8 ⁸ |

* In this table for convenience.

TABLE 5.—THE MOLAR ENTROPY OF SOME LIQUID ALIPHATIC AND ALICYCLIC COMPOUNDS AT 25°C.

| Compound | Formula | Entropy |
|----------------------------------|---------------------------|--------------------|
| <i>n</i> -Pentane | C_5H_{12} | 62.8 ¹⁰ |
| 2-Methylbutane | C_5H_{12} | 60.8 |
| | | 59.5 ¹¹ |
| <i>n</i> -Hexane | C_6H_{14} | 70.6 ¹¹ |
| | | 70.8 |
| | | 69.2 ⁵ |
| 2-Methylpentane | C_6H_{14} | 69.9 ⁵ |
| 2,2-Dimethylbutane | C_6H_{14} | 64.4 ⁵ |
| <i>n</i> -Heptane | C_7H_{16} | 78.6 ¹² |
| 2-Methylhexane | C_7H_{16} | 75.3 |
| 3-Methylhexane | C_7H_{16} | 74.0 |
| 3-Ethylpentane | C_7H_{16} | 74.6 |
| 2,2-Dimethylpentane | C_7H_{16} | 68.1 |
| 2,3-Dimethylpentane | C_7H_{16} | 72.4 |
| 2,4-Dimethylpentane | C_7H_{16} | 69.7 |
| 3,3-Dimethylpentane | C_7H_{16} | 70.1 |
| 2,2,3-Trimethylbutane | C_7H_{16} | 64.8 |
| <i>n</i> -Octane | C_8H_{18} | 86.0 |
| 2,2,4-Trimethylpentane | C_8H_{18} | 78.4 ¹² |

TABLE 5.—THE MOLAR ENTROPY OF SOME LIQUID ALIPHATIC AND ALICYCLIC COMPOUNDS AT 25°C.—(Continued)

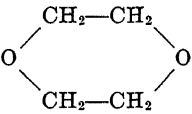
| Compound | Formula | Entropy |
|-----------------------------------|---|---------------------|
| <i>n</i> -Nonane..... | C_9H_{20} | 93.9 |
| <i>n</i> -Decane..... | $C_{10}H_{22}$ | 102.5 |
| <i>n</i> -Undecane..... | $C_{11}H_{24}$ | 110.9 |
| <i>n</i> -Dodecane..... | $C_{12}H_{26}$ | 118.2 |
| Tetradecane..... | $C_{14}H_{30}$ | 134.4 |
| Di-isobutylene (low boil.)..... | $(CH_3)_2C=CH=C(CH_3)_2$ | 73.2 ¹³ |
| (high boil.)..... | $(CH_3)_3C-CH=CH(CH_3)_2$ | 74.5 ¹³ |
| Tri-methylethylene..... | $(CH_3)_2C=CH-CH_3$ | 59.5 |
| Tetra-methylethylene..... | $(CH_3)_2C=C(CH_3)_2$ | 65.1 ¹³ |
| 1,4-Pentadiene..... | C_5H_8 | 58.2 ¹³ |
| Cyclopentane..... | C_5H_{10} | 47.0 ¹¹ |
| Methylcyclopentane..... | $C_5H_9CH_3$ | 59.2 |
| Cyclohexane..... | C_6H_{12} | 49.2 ¹¹ |
| 1,2-Dimethylcyclopentane..... | $C_6H_8(CH_3)_2$ | 64.5 |
| Methylcyclohexane..... | $C_6H_{11}CH_3$ | 59.3 |
| Cyclohexene..... | C_6H_{10} | 51.8 |
| <i>n</i> -Hexene..... | C_6H_{12} | 68.1 |
| Heptene-1..... | C_7H_{14} | 78.6 ¹¹ |
| tert-Butylethylene..... | $C_4H_9-CH=CH_2$ | 61.3 ¹⁴ |
| <i>n</i> -Heptylcyclohexane..... | $C_7H_{15}-C_6H_{11}$ | 106.8 ¹⁵ |
| <i>n</i> -Dodecylcyclohexane..... | $C_{12}H_{25}-C_6H_{11}$ | 147.5 ¹⁵ |
| Methanol..... | CH_3OH | 30.3 |
| Ethanol..... | C_2H_5OH | 38.4 |
| <i>n</i> -Propyl alcohol..... | C_3H_7OH | 46.1 |
| Iso-propyl alcohol..... | C_3H_7OH | 43.0 |
| <i>n</i> -Butyl alcohol..... | C_4H_9OH | 54.5 |
| tert-Butyl alcohol..... | C_4H_9OH | 45.3 |
| <i>n</i> -Amyl alcohol..... | $C_5H_{11}OH$ | 60.9 |
| tert-Amyl alcohol..... | $(CH_3)_2COH-C_2H_5$ | 54.7 |
| <i>n</i> -Hexyl alcohol..... | $C_6H_{13}OH$ | 68.6 |
| Cyclohexanol..... | $C_6H_{11}OH$ | 47.7 |
| Glycol..... | CH_2OH | 39.9 |
| Glycerol..... | CH_2OH | 48.87 ¹⁶ |
| | CH_2OH | |
| | CH_2OH | |
| Dioxane..... | CH_2OH | 47.0 |
| |  | |

TABLE 5.—THE MOLAR ENTROPY OF SOME LIQUID ALIPHATIC AND ALICYCLIC COMPOUNDS AT 25°C.—(*Continued*)

| Compound | Formula | Entropy |
|---------------------------------------|------------------|---------------------|
| Diethyl ether..... | $(C_2H_5)_2O$ | 60.5 |
| Di-isopropyl ether..... | $(C_3H_7)_2O$ | 70.4 |
| Formic acid..... | HCOOH | 33.1 |
| Acetic acid..... | CH_3COOH | 38.0 |
| <i>n</i> -Butyric acid..... | C_3H_7COOH | 54.1 |
| Ethyl acetate..... | $CH_3COOC_2H_5$ | 62.0 |
| Acetone..... | $(CH_3)_2CO$ | 47.9 |
| β -mercapto-propionic acid..... | $SHCH_2CH_2COOH$ | 54.7 |
| Carbon tetrachloride.... | CCl_4 | 52.2 |
| Ethylene dichloride..... | $C_2H_4Cl_2$ | 49.84 ¹⁷ |
| Ethylene dibromide..... | $C_2H_4Br_2$ | 53.37 ¹⁷ |
| <i>n</i> -Butyl bromide..... | C_4H_9Br | 78.22 |
| <i>n</i> -Amyl bromide..... | $C_5H_{11}Br$ | 97.29 |
| <i>n</i> -Hexyl bromide..... | $C_6H_{13}Br$ | 108.33 |
| Methyl amine..... | CH_3NH_2 | 35.90 ¹⁸ |

study of entropy data for such purposes, the available data on the entropies of solid and liquid organic compounds have been incorporated directly in the body of the text. The data have been taken chiefly from Strelkoff's correlation, which is mainly the entropy data for liquids and solids recorded in Parks and Huffman. Additional data have been taken from literature since 1935. The original references have not been included since these may be traced either through the Parks and Huffman monograph or Strelkoff's article. References are given to the additional data taken from the literature since 1935.

By familiarizing himself with these figures, the reader should find it possible to evolve his own set of rules for estimating unknown entropies. If possible, estimates should be made by more than one rule as a check and as a rough criterion of the significance of the value finally adopted for use.

3. The Entropies of Inorganic Solid Compounds.—Following Latimer's success¹⁹ in showing that the entropy of 16 salts could be represented as the sum of the individual contributions from each atom in the compound, a number of semiempirical equations have been prepared for computing the entropies of salts, oxides, and sulphides. These rules have been summarized by Kelley²⁰ in his first survey of the entropies of inorganic compounds.

Latimer's rule gives the entropy contribution at 25°C. for the atom of atomic weight A_1 equal to

$$S_1 = \frac{3}{2}R \ln A_1 - 0.94, \quad (8.4)$$

and hence the entropy of one formula weight of the salt is

$$S = S_1 + S_2 + \cdots = \frac{3}{2}R \ln A_1 A_2 \cdots - n(0.94). \quad (8.5)$$

All of these rules relate the entropy of the compound to $\frac{3}{2}R$ times the logarithm of the product of the atomic weights of the constituent atoms.

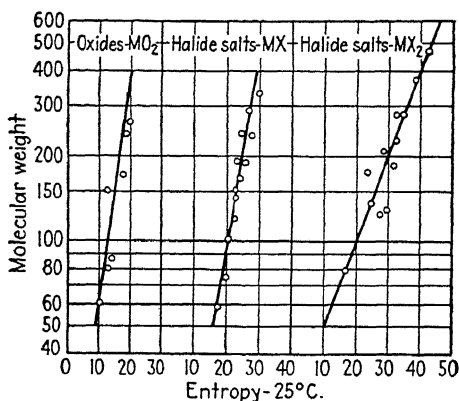


FIG. 9.—The molar entropies of some inorganic solids.

However, as shown by the graphs of Figs. 9 and 10, well-defined straight lines are obtained when the molar entropies at 25°C. are plotted against the molecular weight for each type of compound, instead of the product of the atomic weights. That is, the entropy is given by the empirical relation

$$S = A \log M + B, \quad (8.6)$$

where the constants A and B are the same for the same type compound; in other words, the oxides MO have the same values of A and B , the halide salts MX_2 all have the same values of A and B , etc. On this basis it is possible to make a fair estimate of the entropy of a compound, if the entropies of two compounds of the same type are known so that an entropy-log M plot may be drawn.

Thus, although the entropy of the oxide Cs_2O_4 has not been directly determined, the entropies of the oxides Sb_2O_4 and V_2O_4 are known. By plotting these values against $\log M$, a straight line is drawn from which a rough estimate of 31 units is obtained for the entropy of Cs_2O_4 . Again, in the absence of a direct determination of the entropy of BaO_2 , an estimated value of 15.5 units corresponding to the molecular weight 169.4 may be read from the MO_2 curve (Fig. 9).

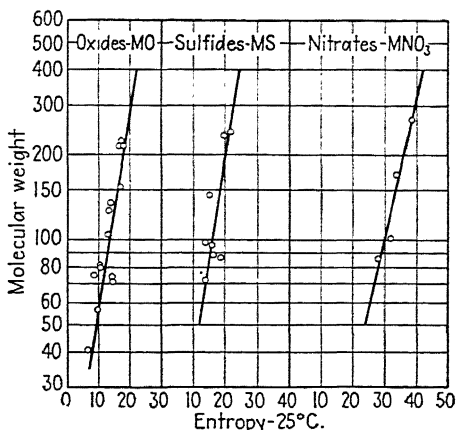


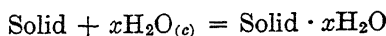
FIG. 10.—The molar entropies of some inorganic solids.

In the case of several salts, the entropy of a hydrated form is available but not the anhydrous compound. Accordingly, the entropy of the anhydrous form was estimated by deducting 10 units for each mole of water of crystallization contained in the hydrated form. Some justification for this procedure may be seen by considering the following pairs of compounds:

| | $S_{298.1}$ | | $S_{298.1}$ | | $S_{298.1}$ |
|--|-------------|---|-------------|---|-------------|
| Asparagine hydrate. | 51.0 | $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | 46.4 | $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 140.5 |
| Asparagine..... | 41.7 | CaSO_4 | 25.5 | Na_2SO_4 | 35.73 |
| Difference..... | 9.3 | | 20.9 | | 104.8 |
| ΔS per mole H_2O . | 9.3 | | 10.5 | | 10.5 |

Apparently each mole of water of crystallization adds about 10 cal./deg. of entropy. A rough estimation of the hypothetical

entropy of solid H_2O at 25°C . gives about 9.4 units, and hence it looks as though the entropy change for the process



is of the order of zero.

When the water enters into chemical combination—as in the hydration of oxides to form bases, or the hydration of organic anhydrides to form solid acids—there appears to be a small decrease in entropy accompanying the addition of hypothetical solid H_2O at 25°C ., as can be seen from a comparison of the following data:

| | $S_{298.1}$ | | $S_{298.1}$ | | $S_{298.1}$ | | $S_{298.1}$ |
|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|--------------------|-------------|
| $\text{Cd}(\text{OH})_2$ | 21.2 | $\text{Ca}(\text{OH})_2$ | 17.4 | $\text{Mg}(\text{OH})_2$ | 15.09 | Phthalic acid | 49.7 |
| CdO | 13.1 | CaO | 9.5 | MgO | 6.66 | Phthalic anhydride | 42.9 |
| Difference | 8.1 | | 7.9 | | 8.43 | | 6.8 |

Until more data become available, the approximate generalization may be made that the addition of H_2O to solid compounds to form solids causes an entropy increase per mole of H_2O of 10, 8.2, and 7 units when the product is a crystalline hydrate, inorganic base, and organic acid, respectively.

For the reader's convenience in estimating unknown entropies, the available entropy data on inorganic solids are presented by type compound in the subsequent tables. These data are taken mainly from the two summaries by Kelley^{20,21} and the literature since 1936. The original references for data found in these two compilations are not included but are given for the later data. Entropies enclosed in parentheses are estimated values. As additional data become available, graphs based on two or three entropies should be redrawn in order to obtain somewhat better average estimates for undetermined entropies. On the whole, it should, with rare exceptions, prove possible to estimate entropies from these charts within about three or four units of the correct value. Since this means an uncertainty in the free energy of less than 1,200 cal. at 25°C ., the uncertainty thereby introduced is probably not much worse than the uncertainty in the older values for the heats of formation of many inorganic compounds.

TABLE 6.—THE ATOMIC ENTROPIES OF SOLID ELEMENTS AT 25°C.

| Element | Atomic weight | Entropy | Element | Atomic weight | Entropy |
|------------------------------|---------------|---------------------|-----------------|---------------|--------------------|
| Al | 26.97 | 6.73 | Ni | 58.69 | 7.1 |
| Sb | 121.76 | 10.5 | Os | 190.2 | 7.8 |
| As | 74.91 | 8.4 | Pd | 106.7 | 8.9 |
| Ba | 137.36 | 15.1 ²² | P (<i>r</i>) | 30.98 | (7) ²² |
| Be | 9.02 | 2.28 | P (<i>w</i>) | 30.98 | 10.6 ²⁶ |
| Bi | 209.00 | 13.60 | Pt | 195.23 | 10.0 |
| B | 10.82 | (1.5) ²² | K | 39.096 | 15.2 |
| Cd | 112.41 | 12.3 | Rh | 102.91 | 7.6 |
| Ca | 40.08 | 9.9 | Rb | 85.48 | 16.6 ²⁶ |
| C (<i>Gr</i>) | 12.01 | 1.36 | Ru | 101.7 | 6.9 |
| C (<i>D</i>) | 12.01 | 0.585 ²³ | Se | 78.96 | 10.0 ²⁶ |
| Ce | 140.13 | 13.8 | Si | 28.06 | 4.5 |
| Cs | 132.91 | 19.8 | Ag | 107.88 | 10.2 |
| Co | 58.94 | 6.8 | Na | 22.997 | 12.2 |
| Cr | 52.01 | 5.68 ²⁴ | Sr | 87.63 | 13.3 ²² |
| Cu | 63.57 | 7.97 | S (<i>Rh</i>) | 32.06 | 7.62 ²⁷ |
| Ga | 69.72 | 10.2 | S (<i>m</i>) | 32.06 | 7.78 ²⁷ |
| Ge | 72.60 | 10.1 | Ta | 180.88 | 9.94 ²⁶ |
| $\frac{1}{2}$ I ₂ | 126.92 | 13.95 | Te | 127.61 | 11.9 ²⁶ |
| Ir | 193.1 | 8.7 | Tl | 204.39 | 15.35 |
| Fe | 55.85 | 6.5 | Sn (<i>w</i>) | 118.70 | 12.3 |
| La | 138.92 | 13.7 | Sn (<i>g</i>) | 118.70 | 10.7 |
| Pb | 207.21 | 15.5 | Ti | 47.9 | 6.6 |
| Li | 6.94 | 6.70 | W | 183.92 | 8.0 |
| Mg | 24.32 | 7.76 | U | 238.07 | 11.1 |
| Mn | 54.93 | 7.61 ²⁵ | V | 50.95 | 7.0 ²⁸ |
| Mo | 95.95 | 6.8 | Zn | 65.38 | 9.95 |

TABLE 7.—THE MOLAR ENTROPIES OF THE OXIDES M₂O AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-------------------|--------------|---------|-------------------|--------------|---------------------|
| Cu ₂ O | 143.14 | 24.0 | Ag ₂ O | 231.76 | 29.09 ²⁹ |

Note: A number of the values given in this chapter were taken from the second revision of inorganic entropies by Kelley,²⁶ which appeared after this manuscript had gone to press.

TABLE 8.—THE MOLAR ENTROPIES OF THE OXIDES MO AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|--------------------|------------------|--------------|--------------------|
| BeO | 25.02 | 3.37 ³⁰ | SrO | 103.63 | 13.0 |
| MgO | 40.32 | 6.66 ³¹ | CdO | 128.41 | 13.1 |
| CaO | 56.08 | 9.5 | SnO | 134.70 | 13.5 |
| MnO | 70.93 | 14.4 | BaO | 153.36 | 16.8 |
| FeO | 71.85 | 14.2 | HgO (<i>r</i>) | 216.61 | 16.5 |
| NiO | 74.69 | 9.21 | HgO (<i>y</i>) | 216.61 | 17.5 |
| CuO | 79.57 | 10.4 | PbO | 223.21 | 16.6 ²⁵ |
| ZnO | 81.38 | 10.4 | | | |

TABLE 9.—THE MOLAR ENTROPIES OF THE OXIDES M₃O₄ AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--------------------------------|--------------|---------|--------------------------------|--------------|---------|
| Mn ₃ O ₄ | 228.79 | 35.5 | Pb ₃ O ₄ | 685.63 | 50.5 |
| Fe ₃ O ₄ | 231.55 | 35.0 | | | |

TABLE 10.—THE MOLAR ENTROPIES OF THE OXIDES M₂O₃ AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--------------------------------|--------------|--------------------|--------------------------------|--------------|--------------------|
| Al ₂ O ₃ | 101.94 | 12.5 | As ₂ O ₃ | 197.82 | 25.6 |
| V ₂ O ₃ | 149.90 | 23.5 ²⁸ | Sb ₂ O ₃ | 291.52 | 29.4 |
| Cr ₂ O ₃ | 152.02 | 19.4 ²⁴ | Bi ₂ O ₃ | 466 | 36.2 ²⁶ |
| Fe ₂ O ₃ | 159.70 | 21.5 | | | |

TABLE 11.—THE MOLAR ENTROPIES OF THE OXIDES MO₂ AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------------------|--------------|---------------------|------------------|--------------|---------|
| SiO ₂ (Q) | 60.06 | 10.1 ²⁸ | SnO ₂ | 150.70 | 12.5 |
| SiO ₂ (Cr) | 60.06 | 10.35 ²⁸ | CeO ₂ | 172.13 | (17.7) |
| SiO ₂ (TR) | 60.06 | 10.5 ²⁸ | PbO ₂ | 239.21 | 18.3 |
| TiO ₂ | 79.9 | 12.45 ³² | ThO ₂ | 264.12 | (19.6) |
| MnO ₂ | 86.93 | 13.9 | | | |

TABLE 12.—THE MOLAR ENTROPIES OF THE OXIDES M_2O_4 AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|--------------------|-----------|--------------|---------|
| V_2O_4 | 165.90 | 24.5 ²⁸ | Sb_2O_4 | 307.52 | 30.4 |

TABLE 13.—THE MOLAR ENTROPIES OF THE OXIDES M_2O_5 AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------|--------------|--------------------|-----------|--------------|--------------------|
| V_2O_5 | 181.90 | 31.3 ²⁸ | Sb_2O_5 | 323.52 | 29.9 |
| As_2O_5 | 229.82 | 25.2 | Ta_2O_5 | 441.76 | 34.2 ²⁸ |

TABLE 14.—THE MOLAR ENTROPIES OF MISCELLANEOUS OXIDES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|---------|----------|--------------|---------|
| WO_3 | 231.92 | (18.3) | U_3O_8 | 842.21 | (72.7) |

TABLE 15.—THE MOLAR ENTROPIES OF THE SALTS MX AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|---------|----------|--------------|--------------------|
| NaCl | 58.454 | 17.3 | KI | 166.016 | 24.1 |
| KCl | 74.553 | 19.75 | AgBr | 187.796 | 25.62 |
| CuCl | 99.027 | 20.8 | CuI | 190.49 | 23.1 |
| NaBr | 102.913 | 20.1 | AgI | 234.80 | 27.6 |
| KBr | 119.012 | 22.5 | TlCl | 239.847 | 25.6 ²⁸ |
| AgCl | 143.337 | 22.97 | TlBr | 284.306 | 26.8 |
| CuBr | 143.486 | 22.8 | TlI | 331.31 | 29.9 |
| NaI | 149.917 | 22.5 | | | |

TABLE 16.—THE MOLAR ENTROPIES OF THE SALTS M_2X_2 AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|------------|--------------|---------|------------|--------------|---------|
| Hg_2Cl_2 | 472.134 | 47.0 | Hg_2Br_2 | 561.052 | 52.8 |

TABLE 17.—THE MOLAR ENTROPIES OF THE SALTS MX_2 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------------|--------------|---------------------|---|--------------|---------------------|
| CaF_2 | 78.08 | 16.4 | $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ | 244.306 | 48.58 ³⁵ |
| CrCl_2 | 122.924 | 27.4 ²⁴ | BaCl_2 | 208.274 | (28.6) |
| FeCl_2 | 126.764 | 29.4 | CdBr_2 | 272.242 | 32.0 ²⁶ |
| ZnCl_2 | 136.294 | 25.9 ²⁶ | PbCl_2 | 278.124 | 32.6 |
| BaF_2 | 175.36 | 23.03 ³⁴ | PbBr_2 | 367.042 | 38.6 |
| CdCl_2 | 183.324 | 31.5 | PbI_2 | 461.05 | 42.2 |
| ZnBr_2 | 225.212 | 33.0 ²⁶ | | | |

TABLE 18.—THE MOLAR ENTROPIES OF THE SALTS MX_3 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------------|--------------|--------------------|-----------------|--------------|---------|
| CrCl_3 | 158.381 | 28.2 ²⁴ | BiCl_3 | 315.371 | 46.0 |
| SbCl_3 | 228.131 | 44.8 | | | |

TABLE 19.—THE MOLAR ENTROPIES OF THE SALTS MXO_3 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|------------------|--------------|--------------------|-----------------|--------------|--------------------|
| KClO_3 | 122.553 | 34.2 | KIO_3 | 214.016 | 36.2 |
| KBrO_3 | 167.012 | 35.7 | AgIO_3 | 282.80 | 37.5 ²⁶ |
| RbClO_3 | 168.937 | 36.3 ²⁶ | | | |

TABLE 20.—THE MOLAR ENTROPIES OF THE SALTS MXO_4 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------------|--------------|---------|------------------|--------------|--------------------|
| KClO_4 | 138.553 | 36.1 | CsClO_4 | 232.367 | 41.9 ³⁴ |

TABLE 21.—THE MOLAR ENTROPIES OF THE CARBONATES $M_2\text{CO}_3$ AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--------------------------|--------------|---------------------|--------------------------|--------------|---------|
| Li_2CO_3 | 73.89 | 21.60 ³⁶ | Ag_2CO_3 | 275.77 | 40.0 |
| Na_2CO_3 | 106.004 | 32.5 | | | |

TABLE 22.—THE MOLAR ENTROPIES OF THE CARBONATES MCO_3 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|---------------------------|--------------|---------|-----------------|--------------|---------|
| MgCO_3 | 84.33 | 15.7 | ZnCO_3 | 125.39 | 19.7 |
| $\text{CaCO}_3(\text{C})$ | 100.09 | 22.2 | SrCO_3 | 147.64 | 23.2 |
| $\text{CaCO}_3(\text{A})$ | 100.09 | 21.2 | CdCO_3 | 172.42 | 25.2 |
| FeCO_3 | 115.86 | 22.2 | BaCO_3 | 197.37 | 26.8 |
| CuCO_3 | 123.58 | 17.7 | PbCO_3 | 267.22 | 31.3 |

TABLE 23.—THE MOLAR ENTROPIES OF THE SULPHATES M_2SO_4 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|---|--------------|---------------------|--------------------------|--------------|---------|
| Li_2SO_4 | 109.94 | 35.3 | K_2SO_4 | 174.252 | 44.8 |
| Na_2SO_4 | 142.054 | 35.73 ³⁷ | Ag_2SO_4 | 311.82 | 47.8 |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 322.214 | 140.5 ²⁶ | Hg_2SO_4 | 497.28 | 47.9 |

TABLE 24.—THE MOLAR ENTROPIES OF THE SULPHATES MSO_4 AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|---|--------------|--------------------|-----------------|--------------|--------------------|
| CaSO_4 (ins.) | 136.14 | 25.5 ⁸⁰ | ZnSO_4 | 161.44 | 30.6 |
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | 172.172 | 46.4 | BaSO_4 | 233.42 | 31.6 |
| CuSO_4 | 159.63 | 25.3 | PbSO_4 | 303.27 | 35.2 ²⁸ |

TABLE 25.—THE MOLAR ENTROPIES OF THE SULPHIDES M_2S AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-----------------------|--------------|---------|-----------------------|--------------|---------|
| Cu_2S | 159.20 | 28.9 | Ag_2S | 247.82 | 35.0 |

TABLE 26.—THE MOLAR ENTROPIES OF THE SULPHIDES MS AT 25°C .

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--------------|--------------|---------|--------------|--------------|---------|
| CaS | 72.14 | 13.5 | ZnS | 97.44 | 13.8 |
| MnS | 86.99 | 18.7 | CdS | 144.47 | (17.0) |
| FeS | 87.91 | 16.1 | HgS | 232.67 | (19.8) |
| CuS | 95.63 | 15.9 | PbS | 239.27 | 21.8 |

TABLE 27.—THE MOLAR ENTROPIES OF THE SULPHIDES MS_2 AT $25^\circ C$.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|--------------------|----------|--------------|--------------------|
| FeS_2 | 119.97 | 12.7 ³⁸ | MoS_2 | 160.07 | 15.0 ³⁸ |

TABLE 28.—THE MOLAR ENTROPIES OF SOME HYDROXIDES AT $25^\circ C$.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|---------|------------|--------------|---------------------|
| $LiOH$ | 23.948 | 12.8 | $Mg(OH)_2$ | 58.336 | 15.09 ³¹ |
| $NaOH$ | 40.005 | 13.8 | $Ca(OH)_2$ | 74.096 | 17.4 ²⁶ |
| | | | $Cd(OH)_2$ | 146.426 | 21.2 |

TABLE 29.—THE MOLAR ENTROPIES OF THE PHOSPHATES $M_3(PO_4)_2$ AT $25^\circ C$.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------------------|--------------|--------------------|----------------|--------------|---------------------|
| $Ca_3(PO_4)_2\alpha$ | 310.20 | 57.6 ³⁹ | $Pb_3(PO_4)_2$ | 811.59 | 84.45 ³⁴ |
| $Ca_3(PO_4)_2\beta$ | 310.20 | 56.4 ³⁹ | | | |

TABLE 30.—THE MOLAR ENTROPIES OF SOME SILICATES AT $25^\circ C$.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-------------|--------------|--------------------|---------------|--------------|--------------------|
| Be_2SiO_4 | 110.10 | 15.4 ⁴⁰ | $Na_2Si_2O_5$ | 182.114 | 39.4 ⁴⁰ |
| Na_2SiO_3 | 122.054 | 27.2 ⁴⁰ | Na_4SiO_4 | 184.048 | 46.8 ⁴⁰ |

TABLE 31.—THE MOLAR ENTROPIES OF THE NITRATES MNO_3 AT $25^\circ C$.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------|--------------|--------------------|----------|--------------|---------------------|
| $NaNO_3$ | 85.005 | 27.8 ²⁶ | $AgNO_3$ | 169.888 | 33.68 ⁴¹ |
| KNO_3 | 101.104 | 31.78 | $TlNO_3$ | 266.398 | 38.4 |

TABLE 32.—THE MOLAR ENTROPIES OF SOME MISCELLANEOUS COMPOUNDS AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--|--------------|---------------------|--|--------------|----------------------|
| Ba(BrO ₃) ₂ ·H ₂ O | 411.208 | 69.0 | MnSe | 133.89 | 21.7 ⁴⁶ |
| Ba(BrO ₃) ₂ | 393.192 | (59.0) | MnTe | 182.54 | 22.4 ⁴⁶ |
| NaHCO ₃ | 84.015 | 24.4 | Ba(NO ₃) ₂ | 261.376 | 51.1 |
| Sm ₂ (SO ₄) ₃ ·8H ₂ O | 733.168 | 161.0 | PCl ₅ | 208.265 | 40.8 ⁴⁷ |
| Sm ₂ (SO ₄) ₃ | 589.04 | (81.0) | IBr | 206.836 | 33.2 |
| AgNO ₂ | 153.888 | 30.62 ⁴² | ICl ₃ | 233.291 | 41.1 |
| Ag ₂ CrO ₄ | 331.77 | 51.82 ⁴³ | PH ₄ I | 161.932 | 32.1 |
| AgClO ₂ | 175.337 | 32.2 ⁴⁴ | NH ₄ Cl | 53.497 | 31.8 |
| CaC ₂ O ₄ ·H ₂ O | 146.116 | 37.3 | TaC | 192.89 | 10.1 ³³ |
| CaC ₂ O ₄ | 128.1 | (27.3) | K ₂ PtCl ₆ | 486.164 | 79.78 ⁴⁸ |
| CaH ₂ | 42.096 | 9.9 | (CH ₃) ₄ NI | 201.064 | 49.7 ⁴⁸ |
| LiH | 7.948 | 6.0 | UO ₂ (NO ₃) ₂ ·6H ₂ O | 502.182 | 120.85 ⁴⁸ |
| KMnO ₄ | 158.026 | 41.04 ⁴⁵ | UO ₂ (NO ₃) ₂ | 394.08 | (60.9) |

4. The Entropies of Gaseous Compounds.—Examination of the data on the entropies of gases at 25°C. discloses a somewhat similar correlation to the one described in Sec. 3 for solids. In this case, however, it is found that plots of the logarithm of the entropy vs. the logarithm of the molecular weight for molecules possessing the same number of atoms yields straight lines. Expressed algebraically,

$$\log S_{298} = A \log M + \log B \quad (8.7)$$

or

$$S_{298} = BM^A, \quad (8.8)$$

where the constants A and B are primarily determined by the number of atoms in the molecule. Entropy-molecular weight plots for molecules containing from 2 to 9 atoms are given in Figs. 11 and 12.

The data on which these correlations are based are given in the following tables. As in the case of solids, the entropies are taken mainly from Kelley's two compilations, plus the literature since 1936. The extension of this type of empirical estimation procedure to long-chain hydrocarbon molecules and gaseous aromatic molecules would probably require some modification in order to allow for the effects of branching and the number of rings in the molecule.

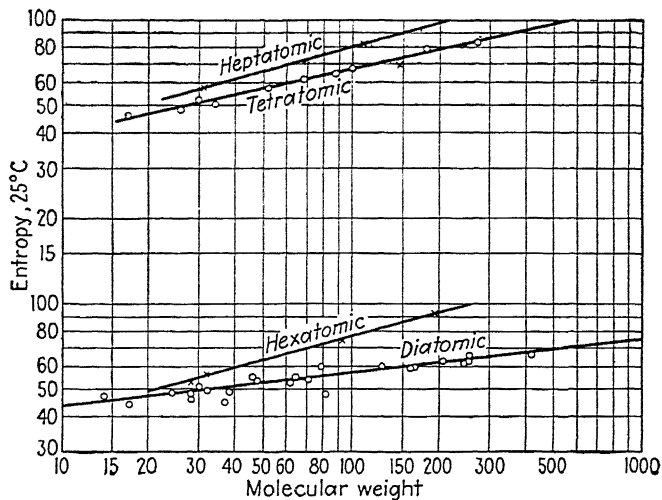


FIG. 11.—The molar entropies of some gaseous molecules.

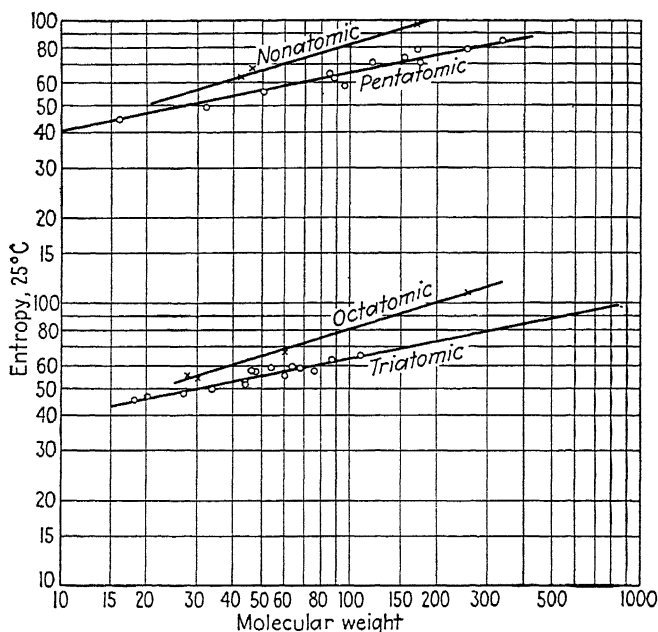


FIG. 12.—The molar entropies of some gaseous molecules.

As is to be expected of correlations which have no foundation in theory, a number of glaring exceptions to the rule exist. For example, in the diatomic classification the entropies of Na_2 , K_2 , Li_2 , and the hydrohalogen molecules deviate by about six or seven units from the curve determined by 22 other diatomic molecules. However since these other molecules range in molecular weight from $2(\text{H}_2)$ to $418(\text{Bi}_2)$ and deviate from the curve by less than two units, the usefulness of the curve is not seriously impaired. Furthermore, the location of the curve for heptatomic molecules is at present uncertain because the two spherical molecules SF_6 and TeF_6 have abnormally low entropies for the correspond-

TABLE 33.—THE MOLAR ENTROPIES OF SOME DIATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|---------------|--------------|--------------------|---------------|--------------|---------------------|
| H_2 | 2.016 | 31.23 | S_2 | 64.12 | 54.41 |
| D_2 | 4.029 | 34.62 | Cl_2 | 70.914 | 53.32 ⁵⁰ |
| Li_2 | 13.88 | 47.01 | K_2 | 78.192 | 59.5 |
| OH | 17.008 | 43.9 | HBr | 80.924 | 47.48 |
| C_2 | 24.02 | 47.9 | Cu_2 | 127.14 | 58.9 ⁵¹ |
| CO | 28.01 | 47.32 | HI | 127.928 | 49.40 |
| N_2 | 28.016 | 45.79 | Br_2 | 159.832 | 58.63 |
| NO | 30.008 | 50.34 | ICl | 162.377 | 59.15 |
| O_2 | 32 | 49.03 | IBr | 206.836 | 62.0 |
| HCl | 36.465 | 44.66 | Sb_2 | 243.52 | 60.9 |
| F_2 | 38 | 48.6 ⁴⁹ | I_2 | 253.84 | 62.29 |
| Na_2 | 45.994 | 54.9 | Te_2 | 255.22 | 64.5 |
| SO | 48.06 | 53.1 | Bi_2 | 418.00 | 65.4 |
| P_2 | 61.96 | 52.0 | | | |

TABLE 34.—THE MOLAR ENTROPIES OF SOME TRIATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------------------|--------------|---------------------|-----------------------|--------------|-----------------------|
| H_2O | 18.016 | 45.13 ⁵¹ | F_2O | 54 | 59.0 |
| D_2O | 20.029 | 47.38 ⁵⁶ | COS | 60.07 | 55.27 ⁵⁶ |
| HCN | 27.026 | 47.92 ⁵² | SO_2 | 64.06 | 59.24 ⁵⁷ |
| H_2S | 34.076 | 49.15 ⁵³ | ClO_2 | 67.457 | 59.6 ⁵⁸ |
| CO_2 | 44.01 | 51.07 ⁵⁴ | CS_2 | 76.13 | 57.1 ⁵⁸ |
| N_2O | 44.016 | 52.58 | Cl_2O | 86.914 | 63.7 ^{26,59} |
| NO_2 | 46.008 | 57.47 ⁵⁵ | NOBr | 109.924 | 65.2 |
| O_3 | 48.0 | 57.1 | | | |

ing molecular weights; consequently, the position of the curve was determined by the two molecules N_2O_5 and CH_3NH_2 . The value for N_2O_5 is not considered too reliable by Kelley.

TABLE 35.—THE MOLAR ENTROPIES OF SOME TETRATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|------------------------|--------------|---|-----------------|--------------|---------------------|
| NH_3 | 17.032 | 45.91 ⁶⁰ 46.034 ⁶¹ | BF_3 | 67.82 | 61.17 ⁶⁶ |
| C_2H_2 | 26.036 | 48.029 ⁶² | PF_3 | 87.98 | 64.2 |
| HCHO | 30.026 | 52.42 ⁶³ | COCl_2 | 98.924 | 67.24 ⁶³ |
| PH_3 | 34.004 | 50.35 ⁶⁴ | AsCl_3 | 181.281 | 78.2 |
| C_2N_2 | 52.036 | 57.64 ⁶⁵ | PBr_3 | 270.728 | 83.4 |

TABLE 36.—THE MOLAR ENTROPIES OF SOME PENTATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|--------------------------|--------------|---------------------|--------------------------|--------------|---------------------|
| CH_4 | 16.042 | 44.5 | CHCl_3 | 119.389 | 70.82 ⁶³ |
| SiH_4 | 32.092 | 48.7 ²⁶ | CCl_4 | 153.838 | 74.05 ⁶⁹ |
| CH_3Cl | 50.491 | 55.94 ⁶⁷ | SiCl_4 | 169.888 | 79.2 |
| CH_2Cl_2 | 84.94 | 64.68 ⁶³ | CH_2Br_2 | 173.858 | 70.84 ⁶³ |
| CF_4 | 88.01 | 62.43 ⁶⁶ | CHBr_3 | 252.766 | 79.14 ⁶³ |
| CH_3Br | 94.95 | 58.61 ⁶⁸ | CBr_4 | 331.674 | 85.59 ⁶³ |

TABLE 37.—THE MOLAR ENTROPIES OF SOME HEXATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|------------------------|--------------|---------------------|------------------------|--------------|---------------------|
| C_2H_4 | 28.052 | 52.48 ⁷⁰ | N_2O_4 | 92.016 | 72.73 ⁵⁵ |
| CH_3OH | 32.042 | 56.63 ⁷¹ | S_6 | 192.36 | 92.2 |

Although the methods described in Secs. 3 and 4 for estimating entropies are highly empirical and, therefore, limited in scope and accuracy, the bulk of the available data for solids and gases indicates that the uncertainty in the estimation of unknown entropies should not exceed three or four units. For most technical purposes this affords sufficient accuracy for arriving at a preliminary picture of the range of temperatures, concentra-

tions, and pressures under which a given reaction can be made to take place. Although such a picture is based on rough thermodynamic data, it is better than no picture at all since, if the mass-

TABLE 38.—THE MOLAR ENTROPIES OF SOME HEPTATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|---------------------------------|--------------|---------------------|------------------|--------------|---------------------|
| CH ₃ NH ₂ | 31.058 | 57.73 ¹⁸ | SF ₆ | 146.06 | 69.43 ⁶⁶ |
| N ₂ O ₅ | 108.016 | 81.8 | TeF ₆ | 241.61 | 80.8 |

TABLE 39.—THE MOLAR ENTROPIES OF SOME OCTATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|-------------------------------|--------------|---------------------|-----------------------|--------------|-------------------|
| B ₂ H ₆ | 27.688 | 55.3 ⁷² | CH ₃ OOC-H | 60.052 | 66.8 ¹ |
| C ₂ H ₆ | 30.068 | 54.85 ⁷³ | S ₈ | 256.48 | 109.2 |

TABLE 40.—THE MOLAR ENTROPIES OF SOME NONATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|----------------------------------|--------------|--------------------|---------------------|--------------|--------------------|
| C ₃ H ₆ | 42.078 | 62.9 ⁷⁴ | Ni(CO) ₄ | 170.73 | 97.0 ⁷⁵ |
| C ₂ H ₅ OH | 46.068 | 66.9 | | | |

TABLE 41.—THE MOLAR ENTROPIES OF SOME DEKATOMIC GASES AT 25°C.

| Compound | Molar weight | Entropy | Compound | Molar weight | Entropy |
|------------------------------------|--------------|---------------------|------------------------------------|--------------|-------------------|
| (CH ₃) ₂ NH | 45.084 | 65.24 ⁷⁶ | (CH ₃) ₂ CO | 58.078 | 70.1 ¹ |

action computations are correctly performed, quantitative relations between the different variables are obtained which are bound to be informative and useful in spite of temperature uncertainties. Since the rate at which reactions can be made

to take place is in many cases more important economically than the extent of the reaction, the information furnished by thermodynamic studies is less important than the laboratory rate and catalyst development studies; therefore, the preliminary thermodynamic analysis should be completed as rapidly as possible.

5. The Heat Capacities of Gaseous Organic Compounds.—

Owing to the preponderance of carbon-hydrogen bonds in the simpler types of organic compounds, it is often possible to compute the heat capacities of gaseous compounds by assigning definite fundamental vibration frequencies to each bond. Values computed in this manner possess adequate accuracy for most technical calculations.

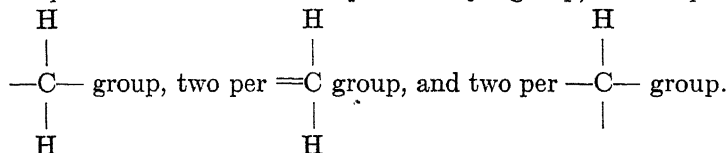
a. Hydrocarbons.—Pitzer⁷⁷ has proposed the following rules for assigning vibration frequencies to gaseous hydrocarbons:

(1) Hydrogen vibrations:

Class A. Stretching of C—H bond distances, one frequency of 3,000 cm^{-1} per H atom.

Class B. Deformation of H—C—H bond angles. Three frequencies of 1,440 cm^{-1} per methyl group and one per methylene group.

Class C. Deformation of H—C—C bond angles. Two frequencies of 950 cm^{-1} per methyl group, three per



(2) Carbon skeleton vibrations:

Class A. Stretching of C—C bonds, a frequency of 1,000 cm^{-1} per bond; and for C=C bonds, a frequency of 1,600 cm^{-1} per bond.

Class B. A bending frequency of 380 cm^{-1} associated with each C—C bond.

(3) Double-bond torsional vibrations:

Class A. A frequency of 570 cm^{-1} per double bond where heavy group is attached to one end of bond.

Class B. A frequency of 270 cm^{-1} per double bond when light (methylene) groups attached at both ends.

The molar-heat capacity is then computed from the relation

$$C_p = 7.95 + \sum_1^{3n-6} RE(x_i), \quad (8.9)$$

where $RE(x_i)$ is the Einstein contribution of the i th fundamental to the vibrational heat capacity.

b. Carbon-hydrogen-oxygen compounds.—Bennewitz and Rossner⁷⁸ have proposed the following rules for assigning vibrational frequencies in the estimation of heat capacities of compounds of this type:

| Bond | Valence (ν) frequency, cm. ⁻¹ | Deformation (δ) frequency, cm. ⁻¹ |
|-----------------|--|---|
| C—C | 990 | 390 |
| C—O (alcohol) | 1031 | 205 |
| C=C | 1620 | 845 |
| C=O (ketone) | 1700 | 390 |
| C—H (aliphatic) | 2920 | 1320 |
| C—H (aromatic) | 3050 | 1320 |
| O—H | 3419 | 1150 |

The method of applying these data to the actual estimation of heat capacities is illustrated by the following problem.

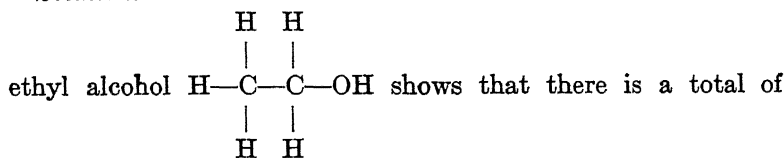
6. Estimation of the Heat Capacity of Gaseous Ethanol.

Illustration 1.—Using the foregoing assignment rules of Bennewitz and Rossner, compute:

a. The vibrational heat capacity of gaseous ethyl alcohol at 300°, 500°, 700°, and 900°K., associated with the valence vibrations ($C\nu$) and with the deformation frequencies ($C\delta$).

b. The total heat capacity at constant pressure at these temperatures.

Solution.—*a.* Examination of the structural formula for



$3 \times 9 - 6 = 21$ fundamentals, of which there are $9 - 1 = 8$ of the so-called valence frequencies; consequently there are 13

deformation frequencies. According to Bennewitz and Rossner's rules, the frequency assignment is as follows:

| Bond | ν , cm. ⁻¹ | δ , cm. ⁻¹ |
|---------|---------------------------|------------------------------|
| C—H (5) | 2920 | 1320 |
| C—C (1) | 990 | 390 |
| C—O (1) | 1031 | 205 |
| O—H (1) | 3419 | 1150 |

Numbers in parentheses represent degeneracies. On the basis of the above assignments, only 8 of the total of 13 deformation fundamentals are accounted for. Bennewitz and Rossner take care of this situation by assuming that the average contribution from the remaining five frequencies is the same as the average of the eight assigned frequencies; consequently the total "deformation heat capacity" is obtained by multiplying the value computed for the eight by $1\frac{3}{8}$. Values of θ_E and θ_E/T corresponding to the above frequencies are recorded below. The corresponding heat capacities are obtained from Table E-1, Appendix 2.

TABLE 42.—THE VIBRATIONAL HEAT CAPACITY OF $C_2H_5OH_{(g)}$

| ω , cm. ⁻¹ | θ | 300°K. | | 500°K. | | 700°K. | | 900°K. | |
|------------------------------|----------|------------|-------|------------|-------|------------|--------|------------|--------|
| | | θ/T | C_v | θ/T | C_v | θ/T | C_v | θ/T | C_v |
| 2,920(5) | 4,184 | 13.947 | 0.002 | 8.368 | 0.162 | 5.977 | 0.907 | 4.649 | 2.095 |
| 990 | 1,419 | 4.730 | 0.399 | 2.838 | 1.057 | 2.027 | 1.426 | 1.577 | 1.622 |
| 1,031 | 1,477 | 4.923 | 0.356 | 2.954 | 1.006 | 2.110 | 1.389 | 1.641 | 1.595 |
| 3,419 | 4,899 | 16.330 | 0.0 | 9.798 | 0.010 | 6.999 | 0.089 | 5.443 | 0.257 |
| C_v | | | 0.757 | | 2.235 | | 3.811 | | 5.569 |
| 1,320(5) | 1,892 | 6.307 | 0.723 | 3.784 | 3.387 | 2.703 | 5.588 | 2.102 | 6.962 |
| 390 | 559 | 1.863 | 1.500 | 1.118 | 1.792 | 0.799 | 1.885 | 0.621 | 1.924 |
| 205 | 294 | 0.980 | 1.835 | 0.588 | 1.930 | 0.420 | 1.958 | 0.327 | 1.969 |
| 1,150 | 1,648 | 5.493 | 0.249 | 3.296 | 0.862 | 2.354 | 1.277 | 1.831 | 1.514 |
| C_δ | | | 4.307 | | 7.971 | | 10.708 | | 12.369 |
| $1\frac{3}{8}C_\delta$ | | | 7.00 | | 12.95 | | 17.40 | | 20.10 |
| $C_{vib.}$ | | | 7.76 | | 15.19 | | 21.21 | | 25.67 |

b. The total molar-heat capacity at constant pressure is obtained by adding the above vibrational heat capacities to the equipartition value (7.95) for translation plus rotation, thus

| | | | | |
|----------------------|-------|-------|-------|-------|
| Temperature, °K..... | 300 | 500 | 700 | 900 |
| C_p | 15.71 | 23.14 | 29.16 | 33.62 |

In computing the heat capacity of ethyl alcohol by this method, the uncertain and difficult question of computing the heat capacity associated with internal rotational degrees of freedom is avoided by treating all internal degrees of freedom as vibrational degrees of freedom. Justification for this procedure is found in the simplicity of the method and the fact that the results are quite accurate. For example, Bennewitz and Rossner give 19.6 cal./(mole)(deg.) for the experimental heat capacity of C_2H_5OH at 410°K., whereas the value obtained from a plot of the above data is 20.0 cal./(mole)(deg.) at this temperature.

7. Other Rules for Heat Capacities.—Parks and Huffman¹ propose the following equation for the heat capacities of the gaseous paraffins:

$$C_p = 4.0 + 1.3n + 0.012nT, \quad (8.10)$$

where n is the number of carbon atoms in the molecule. This relation is a good approximation for $n \geq 3$.

Edmister⁷⁹ proposes the equation

$$C_p = 2.56 + 0.51n + (0.0013n^2 + 0.0044n - 0.00065mn + 0.00495m - 0.0057)T \quad (8.11)$$

for gaseous hydrocarbons, where $n \geq 3$, and m is the number of H atoms in the molecule.

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PART II
APPLICATIONS

CHAPTER IX

ANALYTICAL APPLICATIONS

Thermodynamic considerations may be of assistance in predicting the completeness of a given reaction for analytical purposes. If the reaction of potential analytical interest is of the gravimetric type, the problem may depend on the estimation of the solubility of one or more of the components; if of the volumetric type, an estimate of the degree of completeness of a given oxidation-reduction reaction is apt to be required. Furthermore, potentiometric methods are becoming of increasing importance in the performance of individual analyses and as a basis for continuous control procedures. The subject matter of this chapter may be conveniently divided into the following three topics:

- a. Estimation of solubilities.
- b. Oxidation-reduction reactions.
- c. Potentiometric methods.

Obviously, the last item embraces the first two topics.

1. Estimation of Solubilities.—The application of thermochemical data to the estimation of solubilities in ideal solutions, in regular solutions, and electrolytes in aqueous solutions, is demonstrated by the following three problems. According to Hildebrand, a regular solution is one consisting of nonpolar components which do not associate or form compounds in solution, whereas ideal solutions are characterized by the conformance of each component to Raoult's law. Regular solutions are believed to differ from ideal solutions because the internal pressures of the components differ from each other, and consequently a quantitative measure of this difference is also a measure of the deviation from Raoult's law¹ and ideal behavior.

2. Estimation of Solubilities in Ideal Solutions. *Illustration 1.*
—The molar heat of fusion of *p*-dibromobenzene equals 4,660 cal., and its melting point is 89.3°C.

Calculate the solubility of *p*-dibromobenzene in CS₂ at 25°C. on the assumption that an ideal solution is formed.

Solution.—According to Eq. 5.69, the following relation expresses the temperature dependence of the equilibrium between a pure component and its solution at constant pressure:

$$\frac{d \ln \gamma_2 N_2}{dT} = \frac{\Delta H_2}{RT^2}, \quad (9.1)$$

where ΔH_2 is the heat of fusion of component 2, and the activity coefficient γ_2 is unity for an ideal solution; hence

$$\log \frac{N_2'}{N_2} = \frac{\Delta H_2}{4.575} \left(\frac{1}{T} - \frac{1}{T'} \right). \quad (9.2)$$

At the melting point the mole fraction $N_2 = 1$, $T = 362.4^\circ\text{K}$. Therefore

$$\log N_2' = \frac{1,019}{T'} \left(\frac{T' - 362.4}{362.4} \right).$$

At 298.1°

$$\log N_2' = \frac{1,019}{298.1} \left(\frac{298.1 - 362.4}{362.4} \right) = -0.607.$$

Therefore

$$N_2' = 0.247.$$

The observed mole fraction of *p*-dibromobenzene in CS_2 at 25°C . is 0.224; therefore this solution is almost an ideal one.

3. Estimation of Solubilities in Regular Solutions. *Illustration 2.*—The internal pressures of CS_2 and iodine in the liquid state are known to be sufficiently different so that the solution of the two cannot be ideal. Since both molecules are nonpolar and nonelectrolytes, Hildebrand's treatment for regular solutions may be employed.

Compute the solubility of iodine in CS_2 at 25°C .

Solution.—The following equation is capable of trial-and-error solution when the indicated data on molar volumes and energies of vaporization are available:

$$RT \ln \frac{N_2'}{N_2} = v_2 V_1^2 \left[\left(\frac{\Delta E_2}{v_2} \right)^{1/2} - \left(\frac{\Delta E_1}{v_1} \right)^{1/2} \right]^2, \quad (9.3)$$

where N_2' is the ideal solubility [Eq. (9.2)], and N_2 is the actual solubility. The ΔE 's represent the energies of vaporization of the liquid components at the temperature T , and the v 's are the

corresponding molar volumes. V_1 is the volume fraction of the solvent and is defined by the equation

$$V_1 = \frac{N_1 v_1}{N_1 v_1 + N_2 v_2} = \frac{(1 - N_2) v_1}{(1 - N_2) v_1 + N_2 v_2}. \quad (9.4)$$

Hildebrand uses the value $v_2 = 59.0$ cc. for I_2 at 25°C ., and the corresponding quantity for CS_2 equals $76.13/1.26 = 60.4$ cc. Kelley² gives 11,493 cal. for the ΔH of vaporization of liquid I_2 at 25°C . and 6,682 cal. for liquid CS_2 . The corresponding ΔE 's are obtained by deducting RT from these values, giving 10,900 and 6,090 cal., respectively.

The ideal solubility of I_2 in CS_2 may be computed using Hildebrand and Frederick's³ value of 3,740 cal. for the heat of fusion of I_2 at the melting point and Eq. (9.2). An average value of 3,610 cal. is estimated for ΔH between 25 and 113°C .

$$\log N_2' = \frac{3,610}{1,364} \left(\frac{298.1 - 386.1}{386.1} \right) = -0.602.$$

Therefore

$$N_2' = 0.250.$$

Substituting these data in Eq. (9.3) gives

$$-\log N_2 = 0.547 \left[\frac{(1 - N_2) v_1}{(1 - N_2) v_1 + N_2 v_2} \right]^2 + 0.602.$$

But, since $v_1 \approx v_2$,

$$-\log N_2 = 0.547(1 - N_2)^2 + 0.602.$$

Solving this equation gives $N_2 = 0.088$ for the mole fraction of I_2 in solution in CS_2 at 25°C . The experimental solubility is 0.0576, whereas the value predicted on the assumption of perfect solution is 0.25.

4. Calculation of the Solubility of Electrolytes in Water. *Illustration 3.*—From the entropies of Ag^+ and $\text{CO}_3^{''}$, given in Table 1, Appendix 5, and the heats of formation of these ions, given in Bichowsky and Rossini, compute the solubility of Ag_2CO_3 in water at 25°C .

Solution.—In accordance with the principles discussed in Chap. V, Sec. 8, the difference between the free energy of 1 mole

of Ag_2CO_3 in the hypothetical state of unit activity in solution and the pure solid is

$$\Delta F^\circ_{(aq)} - \Delta F^\circ_{(c)} = RT \ln \frac{1}{a},$$

where a is the activity of Ag_2CO_3 in its saturated solution. If m represents the solubility of Ag_2CO_3 in moles per 1,000 g. H_2O , and γ is the mean ion activity coefficient, then

$$a = (2m\gamma)^2(\gamma m) = 4\gamma^3 m^3.$$

Therefore

$$\Delta F^\circ_{(aq)} - \Delta F^\circ_{(c)} = -1.364 \log 4\gamma^3 m^3.$$

The entropies of Ag^+ and CO_3^{--} are 17.54 and -13.0 units, and the corresponding heats of formation are 25,200 cal. and $-160,500$ cal.; therefore

$$\Delta F^\circ_{(aq)} = 2(25,200) - 160,500 - 298.1[2(17.54) - 13.0 - (95.31)],$$

where the last term in the parentheses represents the entropies of the elements; hence $\Delta F^\circ_{(aq)} = -88,270$ cal.

This value represents the free energy of formation of 1 mole of Ag_2CO_3 in aqueous solution at unity activity from the elements in the standard states.

The free energy of $\text{Ag}_2\text{CO}_{3(c)}$, as computed from the entropy $S_{298.1} = 40.0$ (Table 21, Chap. VIII) and the heat of formation $-119,900$ cal., is

$$\Delta F^\circ_{(c)} = -119,900 - 298.1(40 - 95.31) = -103,410 \text{ cal.}$$

Therefore

$$-88,270 + 103,410 = -1,364 \log 4\gamma^3 m^3.$$

As a first approximation, it may be assumed that the solubility is so low that $\gamma = 1$. Solving this equation for $4m^3$ yields

$$4m^3 = 7.94 \times 10^{-12}$$

or

$$m = 1.26 \times 10^{-4}.$$

Referring to Fig. 19, Appendix 4, it will be noted that no activity coefficients are given for Ag_2CO_3 . However, in this dilute region the data for K_2CO_3 should be applicable; hence a value of 95 per cent is estimated for the mean ion activity coefficient of

Ag_2CO_3 . The solubility is then 1.32×10^{-4} mole per kilogram H_2O .

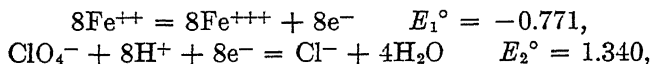
The solubility as computed above implies the complete absence of any CO_2 pressure over the saturated solution, since the solubilities of carbonates increase markedly in the presence of dissolved CO_2 .

5. Oxidation-reduction Reactions.—The possibility of using a given oxidation-reduction reaction as a primary analytical reaction or as a secondary reaction may be evaluated in a preliminary way, with the help of standard free energies of formation or the values for standard oxidation-reduction potentials compiled by Latimer.⁴ It is important to recall that tabulated values for electromotive forces refer to all substances in the hypothetical state of unit activity and fugacity, and that the sign of an electromotive force may be reversed by concentration changes. For this reason it is advisable to first set up an equation for the net electromotive force of a given oxidation-reduction reaction in terms of the standard potential and the concentrations of the substances involved. If the net electromotive forces—obtained by substituting estimated values for concentrations and activity coefficients at the beginning and end of the analysis—are positive, the reaction is at least thermodynamically possible within the range of concentrations visualized.

In spite of the fact that the electromotive force of a reaction is, positive, the actual rate of the reaction at ordinary temperatures and concentrations in the absence of specific catalysts may be so small as to render the reaction useless for analytical purposes. For example, the oxidation of Fe^{++} to Fe^{+++} by means of perchloric acid, in accordance with the equation



may be regarded as the sum of the two half-cell reactions



where the standard potentials have been taken from Latimer's compilation. Thus the standard potential corresponding to reaction (9.5) is +0.569 volt at 25°C ., and the reaction should take place from left to right at unit concentrations.

Actually, perchloric acid does not oxidize ferrous ion rapidly at concentrations around one molal. However, from the equation

$$E = 0.569 - \frac{0.059}{8} \log \frac{(\text{H}_2\text{O})^4(\text{Cl}^-)(\text{Fe}^{+++})^8}{(\text{ClO}_4^-)(\text{H}^+)^8(\text{Fe}^{++})^8}, \quad (9.6)$$

it can be seen that E will increase rapidly with increasing HClO_4 concentration; as a matter of fact, from the equilibrium standpoint—as well as the rate standpoint—this reaction is very favorable in concentrated solutions.

6. Potentiometric Methods.—In the foregoing brief discussion of oxidation-reduction reactions, no mention has been made of the method employed for detecting the end point of the reaction. Since the potential of a given oxidation-reduction reaction is a definite function of the concentrations of the reduced and oxidized components of the system [Eq. (9.6)], it is only necessary to measure the electromotive force of a cell in which the reaction can be made to take place in order to follow the approach of the reaction to the end point, with the addition of titrating reagent.

Furthermore, a number of electrodes are known which are composed of slightly soluble compounds and are reversible with respect to the negative ion of the compound. The use of such an electrode in conjunction with a reference electrode furnishes a convenient means for detecting the end point of titrations involving the precipitation of the electrode compound. The principles involved in the potentiometric titration of precipitation reactions are illustrated by the following problem.

7. Potentiometric Titration of Halogen. *Illustration 4.*—*a.* Devise a cell for the determination of halogen by titration with standard silver nitrate solution. *b.* Show arithmetically how the electromotive force of this cell will vary in the neighborhood of the end point.

Solution.—*a.* The following cell may be used to indicate the change in chloride ion concentration of the unknown solution, as the standard silver nitrate solution is added:

$\text{Ag}; \text{AgCl}, \text{NaCl}(x)_a: (\text{saturated}) \text{KCl}, \text{KCl}(0.1N)\text{HgCl}; \text{Hg}.$

b. The electromotive force of this cell is given by the expression

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{(\text{Cl}^-)} + E_{(1)} - E_{(0.1e)}. \quad (9.7)$$

At 25°C. this becomes

$$E = -0.2222 + 0.059 \log (\text{Cl}^-) + E_{(j)} + 0.3354.$$

Since the liquid junction potential $E_{(j)}$ is small and approximately constant during the titration, and the change of E with extent of reaction is required, this term may be neglected. Therefore

$$E = 0.1132 + 0.059 \log (\text{Cl}^-). \quad (9.8)$$

If the titration cell originally contained n_0 moles of NaCl in V_0 liters of solution, then

$$V = V_0 + cn,$$

where n equals the total moles AgNO_3 added at any stage of the titration, and V is the total liters of solution phase. Since dilute solutions are usually employed in volumetric analysis, it will be satisfactory to substitute concentrations in moles per liter for activities. The constant c equals the reciprocal of the normality of the AgNO_3 solution. Then, total moles

$$\text{Cl}^- = n_0 = (\text{Cl}^-)V + \text{moles precipitated},$$

and total moles $\text{Ag}^+ = n = \text{moles Ag}^+ \text{ in solution plus moles precipitated}$. Subtracting these two equations gives

$$n_0 - n = (\text{Cl}^-)(V) - (\text{Ag}^+)V,$$

where Ag^+ equals the concentration of silver ion in solution. But

$$K = (\text{Ag}^+)(\text{Cl}^-), \quad (9.9)$$

where K equals the solubility product for AgCl at 25°C. Consequently

$$(\text{Cl}^-)^2 - \left(\frac{n_0 - n}{V} \right) (\text{Cl}^-) - K = 0.$$

Therefore

$$(\text{Cl}^-) = \frac{1}{2} \left(\frac{n_0 - n}{V} \right) \pm \frac{1}{2} \sqrt{\left(\frac{n_0 - n}{V} \right)^2 + 4K}. \quad (9.10)$$

Substituting this value for (Cl^-) in Eq. (9.8) gives

$$E = 0.1132 + 0.059 \log \left[\frac{1}{2} \left(\frac{n_0 - n}{V_0 + cn} \right) \pm \frac{1}{2} \sqrt{\left(\frac{n_0 - n}{V_0 + cn} \right)^2 + 4K} \right]. \quad (9.11)$$

Substituting $x = n/n_0 =$ fractional degree of completeness of reaction at any stage of the titration, in Eq. (9.11), yields

$$E = 0.1132 + 0.059 \log \left[\frac{n_0}{2} \left(\frac{1-x}{V_0 + cn_0x} \right) \pm \frac{1}{2} \sqrt{n_0^2 \left(\frac{1-x}{V_0 + cn_0x} \right)^2 + 4K} \right]. \quad (9.12)$$

If $n_0 = 2 \times 10^{-3}$ mole NaCl, $V_0 = 0.020L$, $K = 1.7 \times 10^{-10}$, and $c = 10$ for $0.1N$ AgNO₃; then Eq. (9.12) may be used to compute the change in E near the end point.

| 100x, per cent completeness | E | $-\frac{\Delta E}{\Delta(100x)}$ |
|-----------------------------|---------|----------------------------------|
| 95 0 | -0.0398 | |
| 97.0 | -0.0528 | 0.0065 |
| 98.0 | -0.0636 | 0.0108 |
| 99.0 | -0.0816 | 0.0180 |
| 99.5 | -0.0998 | 0.0364 |
| 99 99 | -0.1698 | 0.143 |

Examination of the above figures shows that, on titrating from 95 to 97 per cent completion, the change in electromotive force per 1 per cent increase is only 6.5 millivolts; in going from 97 to 98 per cent, the change is 11 millivolts per 1 per cent; from 98 to 99, the change is 18 millivolts; and on going from 99 to 99.5 per cent completion, the change in electromotive force is 36 millivolts per 1 per cent increase in completion of the titration. Thus the sharp rate of change of the electromotive force of this cell, accompanying the addition of AgNO₃, in the neighborhood of the end point provides an accurate means for detecting the end point of the reaction.

8. Potentiometric Acidimetry.—An apparatus and procedure similar to that described in illustration 4 may be used to detect the end point of acid-base titrations. In this case the titration cell might consist of the following arrangement of electrodes:

(Pt)H₂; unknown solution: (saturated)KCl, KCl(0.1N)HgCl;
Hg. (9.13)

The electromotive force of this cell is given by the equation

$$E = -\frac{RT}{NF} \ln \frac{(H^+)}{P_{H_2}^{1/2}} + E_{(1)} - E_{(0.1e)}.$$

If $P_{H_2} = 1$ atm., this equation becomes

$$E = -\frac{2.303RT}{NF} \log (H^+) + E_{(L)} - E_{(0.1c)}. \quad (9.14)$$

Owing to the uncertain value of $E_{(L)}$ with the nature of the unknown solution, it is customary to lump $E_{(L)}$ with the potential of the reference half cell; consequently

$$E = -\frac{2.303RT}{NF} \log (H^+) + E_R. \quad (9.15)$$

It may be shown by computations similar to the above that, except for the titration of very weak acids with very weak bases, the electromotive force of this cell varies sharply with (H^+) in the neighborhood of the end point, and hence provides an accurate means for detecting the end point of acid-base titrations.

Equation (9.15) may also be employed to evaluate the pH of a solution. According to the modern technique of measurements, the pH of a solution is defined in terms of the electromotive force of the cell employed to measure the pH of the solution. Thus, rewriting Eq. (9.15) gives

$$E = \left(\frac{2.303RT}{F} \right) pH + E_R \quad (9.16)$$

or

$$pH = \frac{E - E_R}{\frac{2.303RT}{F}}. \quad (9.17)$$

In this equation E is the observed electromotive force of the cell (9.13); and E_R is a constant for the 0.1*N* calomel electrode plus salt bridge, which may be evaluated from electromotive-force measurements on acetic acid-sodium acetate buffers. The evaluation of the constant E_R is carried out so that values of pH computed from Eq. (9.17) have very nearly the significance

$$pH = -\log C_{H^+} \gamma_{\pm}, \quad (9.18)$$

where C_{H^+} represents the stoichiometric concentration of H^+ , and γ_{\pm} is the mean ion activity coefficient.

The method for evaluating E_R is described in detail by MacInnes.⁵ When the 0.1*N* calomel electrode is used as a reference electrode in conjunction with the hydrogen electrode, E_R equals 0.3358 volt at 25°C. and is constant within 0.1 per cent in the range 15 to 38°C. When the quinhydrone electrode is used in

conjunction with the 0.1*N* calomel electrode, E_R is -0.3636 volt at 25°C . and varies appreciably with temperature.

The use of thermochemical data in the development of continuous controls for plant operations, in which a continuous record of acidity is required, is illustrated by the following problem.

9. Design of Continuous Acid Control. *Illustration 5.*—It is required to install a potentiometric device for continuously recording the acidity of a dilute solution of hydrochloric acid, leaving a unit in which hydrogen chloride is absorbed in water. The concentration of HCl in the effluent must be maintained between 15.5 (5*m*) and 16.7 (5.5*m*) weight per cent. The control is to be in operation all year round, at temperatures ranging from 15 to 30°C .; but thermostating of the unit is impossible. The choice between a chemical and concentration cell may therefore be based on the evaluation of the following items:

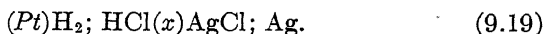
a. Nature of electrodes required for a chemical cell, and electrodes required for a concentration cell.

b. Sensitivity, *i.e.*, millivolts change in electromotive force of the two types of cells within the allowable range of concentration fluctuations.

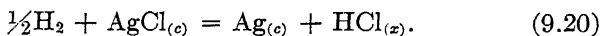
c. Temperature coefficient of electromotive force of the two types of cells.

d. General considerations regarding ruggedness of electrodes, auxiliary equipment, etc., for each type of cell.

Solution.—*a.* A possible chemical cell,



Change of state per faraday,

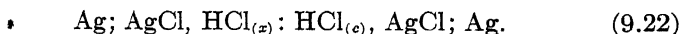


Therefore

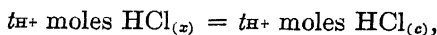
$$E_1 = E^\circ - \frac{RT}{F} \ln \frac{(H^+)(Cl^-)}{P_{H_2}^{1/2}} = E^\circ - \frac{2RT}{F} \ln m\gamma_{\pm} \quad (9.21)$$

for $P_{H_2} = 1$ atm.

A possible concentration cell,



Change of state per faraday,



where t_{H^+} is the transference number of the hydrogen ion. Therefore

$$E_2 = -t_{H^+} \frac{RT}{F} \ln \frac{(H^+)(Cl^-)_{c_2}}{(H^+)(Cl^-)_{x_2}} = -2t_{H^+} \frac{RT}{F} \ln \frac{(m\gamma_{\pm})_{c_2}}{(m\gamma_{\pm})_{x_2}} \quad (9.23)$$

b. The potential of the first cell may be estimated for 5*m* and 5.5*m* HCl at 25°C., by estimating γ_{\pm} equal 2.2 and 2.4 at these two concentrations from the data of Fig. 19, Appendix 4. Consequently

$$\begin{aligned} E_1 &= 0.2222 - 2(0.059) \log 5(2.2) = 0.0992 \text{ volt,} \\ E_1' &= 0.2222 - 2(0.059) \log 5.5(2.4) = 0.0902 \text{ volt,} \\ \text{Max. } \Delta &= 0.0090 \text{ volt.} \end{aligned}$$

The potential of the second cell may be estimated for these two acid concentrations by assuming t_{H^+} constant at 0.76 in this concentration range. If the HCl concentration in the reference cell is 5.25*m*, then

$$\begin{aligned} E_2 &= -(2)(0.76)(0.059) \log \frac{5.25(2.3)}{5.00(2.2)} = -0.00376 \text{ volt} \\ E_2' &= -(2)(0.76)(0.59) \log \frac{5.25(2.3)}{5.5(2.4)} = +0.00340 \text{ volt} \\ \Delta &= 0.00716 \end{aligned}$$

Thus, the chemical cell offers some advantage in that the maximum variation in electromotive force in the allowable concentration range is 9 millivolts compared to 7 millivolts for the concentration cell.

c. The temperature coefficients dE/dT for these two cells may be estimated as follows:

Using the required entropy data from the various tables in the text, ΔS for reaction (9.20) taking place in the chemical cell is

$$\Delta S = 13.5 + 10.2 - 22.97 - 15.62 = -14.89.$$

From the relation

$$\begin{aligned} \Delta S &= F \frac{dE}{dT} \\ \frac{dE}{dT} &= -\frac{14.89}{23,066} = -6.45 \times 10^{-4} \text{ volt/deg.} \end{aligned}$$

Although this calculation corresponds to the temperature coefficient of a cell containing HCl at unit activity, this value is approximately correct for 5*m* acid.

The temperature coefficient of the concentration cell may be estimated from the relation

$$\frac{dE}{dT} = \frac{\Delta H}{TF} + \frac{E}{T}$$

and the enthalpy data contained in illustration 1, Chap. III. Referring to Table 2, Chap. III, it will be noted that the relative partial molar-heat content of HCl in 5.5*m* acid is about 2,630 cal.; and in 5.25*m* acid, it is about 2,530 cal. Hence ΔH for this cell process is approximately $2,530 - 2,630 = -100$ cal./mole transferred, or -76 cal. for the actual amount transferred. Therefore

$$\frac{dE}{dT} = -\frac{76}{(298.1)(23,066)} - \frac{0.00340}{298.1} = -2.24 \times 10^{-5} \text{ volt/deg.}$$

It will be noticed that the concentration cell has a decided advantage in the absence of a thermostat, since its temperature coefficient is of the order of 0.02 millivolt/deg. compared with 0.6 millivolt/deg. for the chemical cell.

d. The concentration cell has the additional advantages that two fairly rugged silver chloride electrodes may be used, whereas the chemical cell requires a hydrogen electrode with tank hydrogen and auxiliary flow controls. Furthermore, the potential of this cell varies with changes in the H_2 pressure, due to the influence of temperature on the vapor pressure of the test solution. On the whole, the advantage appears to be with the concentration cell, rather than with the chemical cell, for the requirements of this particular job; and in the absence of a thermostat the chemical cell would be quite useless.

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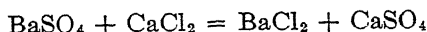
CHAPTER X

INDUSTRIAL CHEMICALS

The use of thermochemical data in the development of chemical processes and as a guide in plant operations is illustrated by the following set of problems.

1. Barium Chloride from Barite and Calcium Chloride. *Illustration 1.*—The possibility of obtaining BaCl_2 by fusing barite (BaSO_4) with CaCl_2 has been investigated in the laboratory¹ around 1600°F.

Derive equations for the ΔH and ΔF° of the reaction



at elevated temperatures, and compute the BaSO_4 conversions at 1600°F. for $r_0 = 1$ and $r_0 = 2$ (see page 212).

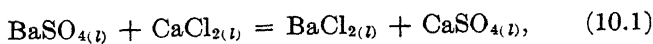
Solution.—The following thermal data are required for this problem:

| Compound | $S_{298.1}$ | ΔH , formation | Melting point °K. | ΔH , fusion | C_p (solid) |
|-----------------|-------------|---------------------------|----------------------|------------------------|--|
| CaCl_2 | 22.0* | -190,600 | 1055 | 6100 | $16.9 + 3.86 \times 10^{-3}T$ |
| CaSO_4 | 25.6 | -340,700 | 1570 | 6700 | $18.52 + 21.97 \times 10^{-3}T - \frac{1.57 \times 10^5}{T^2}$ |
| BaCl_2 | 28.6* | -205,280 | 1233 | 5370 | $17.0 + 3.34 \times 10^{-3}T$ |
| BaSO_4 | 31.5 | -349,400 | 1623 | 9700 | $21.35 + 14.1 \times 10^{-3}T$ |

* Estimated.

The foregoing data on heats of fusion, melting points, and heat capacities have been taken from the compilations of Kelley, already cited. Entropies are taken from the tabulations of Sec. 3, Chap. VIII, and the entropy of CaCl_2 has been estimated from its molecular weight and the graphs of Fig. 9, Chap. VIII.

The reaction occurring in the melt is



and the equilibrium constant is

$$K = \frac{(\text{BaCl}_2)(\text{CaSO}_4)}{(\text{BaSO}_4)(\text{CaCl}_2)}, \quad (10.2)$$

where the parentheses represent activities. In the absence of data on ionization or activity coefficients for this system, the simplest assumption of activities proportional to mole fractions and no ionization is valid. If the reaction mass originally consisted of n_1 moles of BaSO_4 plus n_2 moles of CaCl_2 , and if $100x$ represents the mole per cent BaSO_4 converted at equilibrium, then the individual mole fractions at equilibrium would be

$$\begin{aligned} N_{\text{BaSO}_4} &= \frac{n_1(1-x)}{n_1+n_2} \\ N_{\text{CaCl}_2} &= \frac{n_2-n_1x}{n_1+n_2} \\ N_{\text{BaCl}_2} &= \frac{n_1x}{n_1+n_2} \\ N_{\text{CaSO}_4} &= \frac{n_1x}{n_1+n_2} \end{aligned}$$

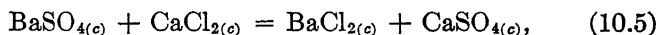
Substituting these values in 10.2 yields

$$K = \frac{n_1x^2}{(1-x)(n_2-n_1x)} = \frac{x^2}{(1-x)(r_0-x)}, \quad (10.3)$$

where r_0 = initial mole ratio CaCl_2 to BaSO_4 ; therefore

$$x = \frac{(r_0+1)K \pm [(r_0+1)^2K^2 - 4(K-1)(r_0K)]^{1/2}}{2(K-1)}. \quad (10.4)$$

In order to compute K , it is necessary to evaluate ΔF° for reaction (10.1) at $1623^\circ\text{K}.$, with the substances in the standard states indicated by that equation. For the reaction



$$\Delta S_{298.1} = 28.6 + 25.6 - 22.0 - 31.5 = 0.7$$

$$\Delta H_{291.1} = -5,980 \simeq \Delta H_{298.1}$$

$$\Delta F_{298.1}^\circ = -5,980 - 209 = -6,190 \text{ cal.}$$

$$\Delta C_p = -2.73 + 7.35 \times 10^{-3}T - 1.57 \times 10^{-5}T^{-2}$$

$$\begin{aligned} \Delta H &= -6,036 - 2.73T + 3.68 \times 10^{-3}T^2 \\ &\quad + 1.57 \times 10^{-5}T^{-1}. \end{aligned} \quad (10.6)$$

Substituting (10.6) in (5.12) gives

$$d\left(\frac{-\Delta F^\circ}{T}\right) = \left(\frac{-6,036}{T^2} - \frac{2.73}{T} + 3.68 \times 10^{-3} + \frac{1.57 \times 10^5}{T^3}\right) dT$$

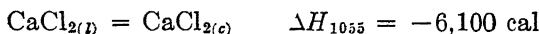
$$-\Delta F^\circ = 6,036 - 6.29T \log T + 3.68 \times 10^{-3}T^2 - 0.785 \times 10^5 T^{-1} + 15.9T. \quad (10.7)$$

At 1055°K., ΔH and ΔF° , as computed from (10.6) and (10.7), are

$$\Delta H_{1055} = -4,667 \text{ cal.}$$

$$\Delta F^\circ_{1055} = -6,762 \text{ cal.}$$

But for the process



Hence, for the standard states in the following equation:



$$\Delta H_{1055} = -10,767 \text{ cal.}$$

$$\Delta F^\circ_{1055} = -6,762 \text{ cal.}$$

Since no data are available on the heat capacities of the liquid components of this system, it will be assumed that ΔC_p is the same function of temperature regardless of state. Consequently, above 1055°K.,

$$\Delta H = -12,136 - 2.73T + 3.68 \times 10^{-3}T^2 + 1.57 \times 10^5 T^{-1} \quad (10.9)$$

$$-\Delta F^\circ = 12,136 - 6.29T \log T + 3.68 \times 10^{-3}T^2 - 0.785 \times 10^5 T^{-1} + 10.15T. \quad (10.10)$$

At the melting point of BaCl_2

$$\Delta H_{1233} = -9,780 \text{ cal.}$$

$$\Delta F^\circ_{1233} = -6,242 \text{ cal.}$$

For the process



Hence for the reaction



$$\Delta H_{1233} = -4,410 \text{ cal.}$$

$$\Delta F^\circ_{1233} = -6,242 \text{ cal.,}$$

and for reaction (10.11)

$$\Delta H = -6,777 - 2.73T + 3.68 \times 10^{-3}T^2 + 1.57 \times 10^5T^{-1} \quad (10.12)$$

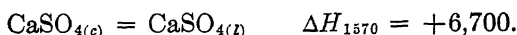
$$-\Delta F^\circ = 6,777 - 6.29T \log T + 3.68 \times 10^{-3}T^2 - 0.785 \times 10^5T^{-1} + 14.47T. \quad (10.13)$$

At the melting point of CaSO_4

$$\Delta H_{1570} = -1,877 \text{ cal.}$$

$$\Delta F^\circ_{1570} = -7,017 \text{ cal.}$$

For the process



Hence for the reaction



$$\Delta H_{1570} = +4,823 \text{ cal.}$$

$$\Delta F^\circ_{1570} = -7,017 \text{ cal.};$$

and for reaction (10.14)

$$\Delta H = -77 - 2.73T + 3.68 \times 10^{-3}T^2 + 1.57 \times 10^5T^{-1} \quad (10.15)$$

$$-\Delta F^\circ = 77 - 6.29T \log T + 3.68 \times 10^{-3}T^2 - 0.785 \times 10^5T^{-1} + 18.70T. \quad (10.16)$$

At the melting point of BaSO_4

$$\Delta H_{1623} = +5,290 \text{ cal.}$$

$$\Delta F^\circ_{1623} = -7,329 \text{ cal.}$$

For the process



Hence for the reaction



$$\Delta H_{1623} = -4,410 \text{ cal.}$$

$$\Delta F^\circ_{1623} = -7,329 \text{ cal.}$$

For reaction (10.17), with all components in the liquid state as standard reference state,

$$\Delta H = -9,777 - 2.73T + 3.68 \times 10^{-3}T^2 + 1.57 \times 10^5T^{-1} \quad (10.18)$$

$$-\Delta F^\circ = 9,777 - 6.29T \log T + 3.68 \times 10^{-3}T^2 - 0.785 \times 10^5T^{-1} + 12.75T. \quad (10.19)$$

The equilibrium constant for Eq. (10.3) may now be calculated for any temperature where it is fairly certain that all components are in the liquid state. At 1144°K ,

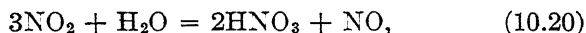
$$-\Delta F^{\circ} = 7,129 \text{ cal; therefore } K = 22.9.$$

Substituting this value in Eq. (10.4) with $r_0 = 1$ gives $x = 0.823$, or 82.3 mole per cent of the BaSO_4 would be converted at equilibrium.

If $r_0 = 2$, then $x = 0.965$, or 96.5 mole per cent of the BaSO_4 would be converted at equilibrium at 1144°K .

It is interesting to note that Shreve and Toner¹ report 82.9 per cent conversion of the BaSO_4 for $r_0 = 1$ and 98.2 per cent conversion for $r_0 = 2$, at this temperature (1600°F). Although ΔF° is favorable for this reaction at lower temperatures, it is doubtful if appreciable reaction will take place at temperatures below those at which all components are liquid, owing to the slow rates of reactions between solid phases. Another interesting point about this reaction is that, since it is mildly exothermic at reaction temperatures, the only heat required for the process is that involved in heating the reactants up to appropriate temperatures. Much of this heat should be recoverable by interchange with the products.

2. Nitric Acid from Nitrogen Oxides. *Illustration 2.*—The strength of nitric acid, produced by the countercurrent absorption of nitrogen oxides in water, is determined, to a large extent, by the equilibria expressed by means of the equations



In order to demonstrate the effect of temperature, total pressure, and gas composition on the maximum concentration of acid obtainable, compute:

a. The equilibrium constants for these two reactions at 25, 35, and 45°C .

b. The maximum concentration of HNO_3 producible at 1 atm. pressure from a gas containing a total mole fraction of oxides equal to 0.07 (70 per cent oxidized) at 25 and 45°C .

c. The maximum concentration producible at 1 atm. and 45°C . with an oxide mole fraction equal to 0.04 (50 per cent oxidized).

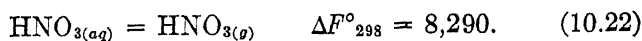
d. The maximum concentration producible at 5 atm. from a gas containing 7 mole per cent oxides (90 per cent oxidized) at 45°C.

Solution.—a. The equilibrium constants corresponding to reactions (10.20) and (10.21) may be computed from the entropies of the substances involved (Chap. VIII) and the necessary heats of formation.

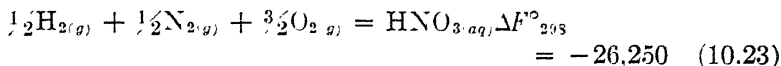
| Compound | $S_{298.1}$ | $\Delta H_{298.1}$ | $\Delta F^{\circ}_{298.1}$ |
|-----------------------------|-------------|--------------------|----------------------------|
| $\text{NO}_{(g)}$ | 50.35 | 21,526 | 20,650 |
| $\text{NO}_{2(g)}$ | 57.47 | 7,964 | 12,275 |
| $\text{N}_2\text{O}_{4(g)}$ | 72.73 | 2,239 | 23,440 |
| $\text{H}_2\text{O}_{(l)}$ | 16.75 | -68,318 | -56,690 |
| $\text{H}_2\text{O}_{(g)}$ | 45.13 | -57,800 | -54,636 |
| $\text{HNO}_{3(aq)}$ | 35.0 | -49,190(B-R) | -26,250 |

NOTE: ΔH data for NO , NO_2 , and N_2O_4 are taken from Giauque and Kemp.²

Inasmuch as activity coefficients of HNO_3 have not been determined in solutions stronger than 27 weight per cent, and the range of acid concentrations of interest is from 30 to 60 weight per cent, the infinitely dilute solution does not constitute a useful or practical reference state for HNO_3 . At ordinary temperatures, vapor pressures of H_2O and HNO_3 over acids in this range of concentration are available (I.C.T., Vol. III), and consequently it will be assumed that the activities of H_2O and HNO_3 at any concentration are measured by their respective partial pressures. Thus, if the standard free energies of formation of H_2O and HNO_3 in an acid of convenient reference concentration may be evaluated, the activities or partial molar free energies in any other concentration may readily be computed from the ratios of the partial pressures of the two components, at the two concentrations in question. In order to do this, it will be necessary to evaluate the standard free energy and heat of formation of $\text{HNO}_{3(g)}$ at 25°C. Lewis and Randall (L-R, p. 567) give the requisite datum for computing the free energy, namely,



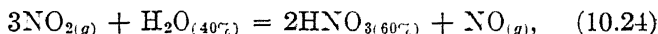
Adding this equation to the equation



gives $\Delta F_{298}^{\circ} = -17,960$ cal. for $\text{HNO}_{3(l)}$.

The heat of formation of this compound is also necessary in order to evaluate equilibriums at higher temperatures. Bichowsky and Rossini give $-41,660$ cal. for the heat of formation of liquid HNO_3 at 18°C . If the heat of vaporization of liquid HNO_3 , $9,130$ cal.—computed from the vapor-pressure data in illustration 4, Chap. V—is added to this value, the heat of formation of gaseous HNO_3 is found to be $-32,530$ cal. at 18°C ., or $-32,560$ cal. at 25°C .

Choosing H_2O and HNO_3 in 60 weight per cent HNO_3 as standard reference states at all temperatures, the free-energy change, corresponding to the reaction



may then be computed from the free energies for the gaseous components and the relations

$$\text{H}_2\text{O}_{(g)} = \text{H}_2\text{O}_{(40\%)}$$

$$\Delta F_{298} = 1,364 \log P_{\text{H}_2\text{O}} = -2,720 \text{ cal.}$$

$$\text{HNO}_{3(g)} = \text{HNO}_{3(60\%)}$$

$$\Delta F_{298} = 1,364 \log P_{\text{HNO}_3} = -3,820 \text{ cal.}$$

Hence the free energy of formation of 1 mole of HNO_3 in 60 weight per cent HNO_3 from the elements in their standard states, at 25°C ., is $-21,780$ cal.; and the free energy of formation of 1 mole of H_2O in 60 per cent HNO_3 is $-57,356$ cal. The difference between the partial molar free energies in the reference state and in any other concentration of practical interest is

$$\Delta F_{\text{HNO}_3} = RT \ln \frac{P\%}{P_{60\%}} = RT \ln a_{\text{HNO}_3} \quad (10.25)$$

$$\Delta F_{\text{H}_2\text{O}} = RT \ln \frac{P\%}{P_{40\%}} = RT \ln a_{\text{H}_2\text{O}}. \quad (10.26)$$

The equilibrium constant corresponding to Eq. (10.24) is

$$K_1 = \frac{P_{\text{NO}}(\text{HNO}_3)^2}{P_{\text{NO}_2}^3(\text{H}_2\text{O})}, \quad (10.27)$$

where the formulas in parentheses represent activities as defined by Eqs. (10.25) and (10.26). At 25°C., ΔF° for reaction (10.24) equals $-2,380$ cal., and K_1 equals 55.2.

The ΔH of reaction (10.20), with all substances in the gaseous state, may be expressed as function of temperature by estimating $\Delta C_p = -5$ cal.

Therefore

$$\Delta H = -8,196 - 5T. \quad (10.28)$$

Substituting this equation in (5.12) and integrating give

$$\Delta F^\circ = -8,196 + 11.52T \log T + 7.50T. \quad (10.29)$$

Hence

$$\Delta F^\circ_{308.1} = 2,964 \quad \text{and} \quad \Delta F^\circ_{318.1} = 3,349 \text{ cal.}$$

The free-energy change corresponding to Eq. (10.24) is then computed by adding the appropriate ΔF 's, accompanying the transfer to 60 per cent acid, based on known vapor-pressure data. The ΔF 's for reaction (10.24) at 35 and 45°C. are, therefore, $-1,686$ and $-1,021$ cal., respectively.

The problem of evaluating some maximum HNO_3 concentrations, producible by countercurrent contacting of nitric acid with nitrogen oxides, under a variety of operating conditions, may now be attempted with the help of the following equilibrium constants:

| | Temperature | | |
|---|-------------|-------|-------|
| | 25°C. | 35°C. | 45°C. |
| $K_1 = \frac{P_{\text{NO}}(\text{HNO}_3)^2}{P_{\text{NO}_2}^2(\text{H}_2\text{O})}$ | 55.2 | 15.8 | 5.05 |
| $K_2 = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$ | 6.51 | 3.10 | 1.56 |

The equilibrium constants, K_2 , have been computed from the equation

$$\Delta F^\circ = -13,693 + 42.21T. \quad (10.30)$$

b. Assume that the absorption system is operating under a substantially constant total pressure of P atm., and let

n_n = pound moles oxides (monomers) entering absorption system per hour.

n_0 = pound moles oxygen entering absorption system per hour.

n_i = pound moles N_2 , plus H_2O , entering absorption system per hour.

x = fraction of total oxides present in an oxidation state of plus four (NO_2 or N_2O_4)

$$x = \frac{\text{moles } NO_2 + 2(\text{moles } N_2O_4)}{NO + NO_2 + 2N_2O_4}.$$

y = fraction total NO_2 present associated to N_2O_4 .

Therefore

$$P_{NO} = N_n(1 - x)P \quad (10.31)$$

$$P_{NO_2} = N_n x(1 - y)P \quad (10.32)$$

$$P_{N_2O_4} = \frac{N_n}{2} xyP, \quad (10.33)$$

where

$$N_n = \frac{n_n}{n_n \left(1 - \frac{xy}{2}\right) + n_0 + n_i} \quad \cdot$$

= total mole fraction of oxides. (10.34)

Substituting these expressions for the individual oxide pressures in K_1 and K_2 gives

$$\frac{K_1}{\rho} = \frac{(1 - x)}{N_n^2 x^3 (1 - y)^3 P^2}, \quad (10.35)$$

where $\rho = \frac{a_{HNO_3}^2}{a_{H_2O}}$

$$K_2 = \frac{y}{2N_n x(1 - y)^2 P}. \quad (10.36)$$

In order to solve these two equations, it is necessary to solve (10.36) for y , corresponding to a given gas composition (N_n and x), and then compute the right-hand side of Eq. (10.35). From a plot of K_1/ρ vs. weight per cent HNO_3 , the acid concentration in equilibrium with specified gas composition is readily determined. Solving Eq. (10.36) gives

$$y = \frac{1}{2}(2 + B) \pm \frac{1}{2}[(2 + B)^2 - 4]^{1/2}, \quad (10.37)$$

where $B = 1/2N_n x P K_2$.

Values of K_1/ρ vs. weight per cent HNO_3 are plotted on Fig. 13 for 25 and 45°C. As explained above, activities have been computed from the relations:

$$a_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}(x \text{ per cent})}{P_{\text{H}_2\text{O}}(60 \text{ per cent HNO}_3)}$$

$$a_{\text{HNO}_3} = \frac{P_{\text{HNO}_3}(x \text{ per cent})}{P_{\text{HNO}_3}(60 \text{ per cent HNO}_3)}$$

If $P = 1$ atm., $N_n = 0.07$ and $x = 0.70$ at 25°C.; then $B = 1.568$; and substituting in (10.37) gives $y = 0.304$.

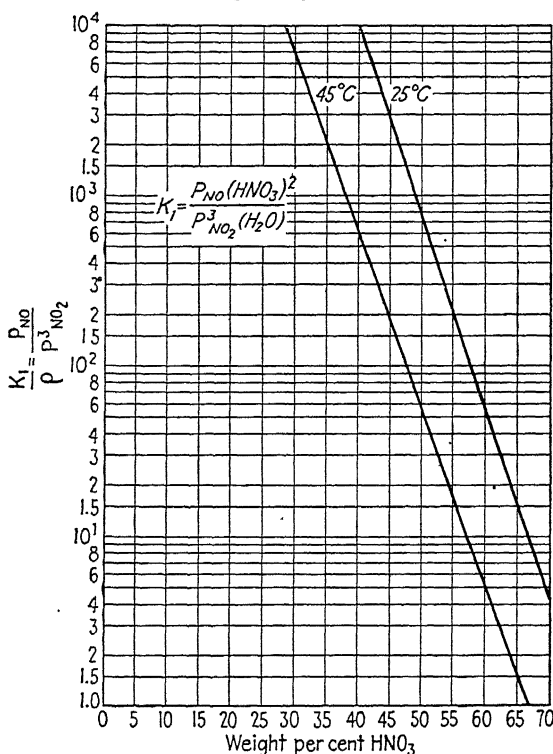


FIG. 13.—The equilibrium between HNO_3 and nitrogen oxides.

Substituting these values in Eq. (10.35) gives

$$K_1/\rho = 5.28 \times 10^2;$$

and from Fig. 13 this corresponds to 51.2 per cent HNO_3 at 25°C.

For 45°C., but otherwise same conditions, $K_2 = 1.56$, and $B = 6.54$; therefore $y = 0.125$ and $K_1/\rho = 267$, and the corresponding equilibrium acid strength is 43.2 weight per cent.

Thus an increase in temperature from 25 to 45°C., for the given gas composition at 1 atm., causes a decrease in maximum HNO_3 concentration from 16.6*m* to 12.1*m*.

c. At 1 atm. and 45°C., with $N_n = 0.04$ and $x = 0.5$, $B = 16$; therefore $y = 0.055$. Consequently $K_1/\rho = 2.96 \times 10^3$, and the equilibrium acid concentration is 33.2 per cent.

d. With $N_n = 0.07$, $x = 0.90$, $T = 45^\circ\text{C.}$, and $P = 5$ atm.,— $B = 1.015$ and $y = 0.378$. Therefore $K_1/\rho = 4.67$, and the maximum acid concentration is 60.0 per cent.

The calculations heretofore given illustrate the way in which thermodynamics may be of service in plant operations. When the gas and liquor compositions, temperature, and pressure are known at the liquor finishing point of the absorption system, it is a relatively simple matter to determine whether or not the system is producing as strong an acid as it should for the given operating conditions, from known thermochemical data.

3. Nitroparaffins. *Illustration 3.*—a. Estimate the free energies of formation of nitromethane and nitroethane at 25°C.

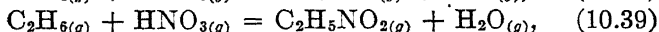
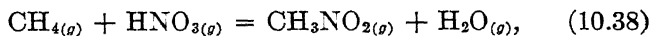
b. Indicate the conditions of temperature and pressure likely to be favorable to the formation of these compounds, from the corresponding hydrocarbons and gaseous HNO_3 .

Solution.—a. From the graphs of Fig. 11, Chap. VIII, the molar entropies of gaseous CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ at 25°C. are estimated to be 68.0 and 76.0 units, respectively. The heats of formation of the gaseous compounds (B-R) are $-18,600$ and $-23,000$ cal./mole, respectively. Accordingly, the standard free energies of formation are

$$\text{CH}_3\text{NO}_{2(g)}: \Delta F^\circ_{298} = -18,600 - 298.1(-52) = -3,100 \text{ cal.}$$

$$\text{C}_2\text{H}_5\text{NO}_{2(g)}: \Delta F^\circ_{298} = -23,000 - 298.1(-76.7) = -100 \text{ cal.}$$

b. The free-energy change for the nitration reactions



may be evaluated from the known ΔH 's and ΔF 's for methane and ethane^{3,4} and the values for $\text{HNO}_{3(g)}$ given in the previous problem.

For reaction (10.38),

$$\begin{aligned}\Delta F^\circ_{298} &= -54,636 - 3,100 + 17,960 + 12,085 = -27,691 \\ \Delta H_{298} &= -57,800 - 18,600 + 32,560 + 17,865 = -25,975.\end{aligned}$$

Therefore

$$\Delta F^\circ = -25,975 - 5.76T. \quad (10.40)$$

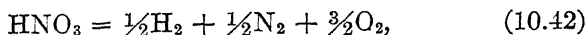
For reaction (10.39),

$$\begin{aligned}\Delta F^\circ_{298} &= -54,636 - 100 + 17,960 + 7,787 = -28,990 \\ \Delta H_{298} &= -57,800 - 23,000 + 32,560 + 20,191 = -28,050.\end{aligned}$$

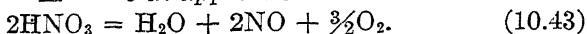
Therefore

$$\Delta F^\circ = -28,050 - 3.15T. \quad (10.41)$$

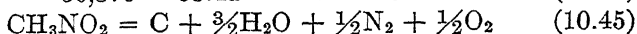
Thus, reactions (10.38) and (10.39) are accompanied by large favorable free-energy changes at all temperatures; consequently the yields obtained from these reactions are not determined by equilibrium conditions but by kinetic factors and catalytic influences. The effect of pressure on these reactions must therefore be related to its effect on kinetic factors, such as concentrations, times of retention, etc. Nevertheless, thermodynamics does afford some positive information which is of definite value in predicting favorable conditions for performing these reactions, as can be seen from a consideration of the following gas-phase reactions:



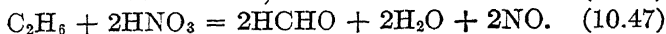
$$\Delta F^\circ = 0 \text{ at approx. } 394^\circ\text{C.}$$



$$\Delta F^\circ = 50,370 - 93.4T \quad \Delta F^\circ = 0 \text{ at } 270^\circ\text{C.} \quad (10.44)$$



$$\Delta F^\circ = -68,000 - 36.6T. \quad (10.46)$$



$$\Delta F^\circ = -42,630 - 112T. \quad (10.48)$$

Owing to the inherent inertness of the paraffin hydrocarbons to chemical attack, reactions (10.38) and (10.39) would not be expected to occur at temperatures appreciably below 400°C. ; at these temperatures the HNO_3 is extremely unstable with respect to decomposition into elements or NO [Eq. (10.42) to (10.44)]. Consequently, unless conditions are such that the rates of the

primary reactions (10.38) and (10.39) are much faster than the rates of (10.42) or (10.43), so that the HNO_3 reacts fruitfully, considerable loss of fixed nitrogen may occur. Furthermore, the nitroparaffins are highly unstable with respect to decomposition into H_2O , N_2 , etc. (10.46), and oxidation to formaldehyde is very favorable, as shown by Eq. (10.48). The free-energy change for the oxidation to CO and CO_2 would be still larger, and hence these secondary products would also be formed to some extent.

On the basis of these considerations, it would appear that the efficient conversion of HNO_3 to nitroparaffins is largely a question of the relative rates of the various reactions discussed above. The efficiency of such a reaction system is usually sharply dependent on temperature, concentrations, and time of retention in the reaction vessel, as well as chance catalytic influences. Hibshman, Pierson, and Hass⁵ have found that the efficiency of utilization of the HNO_3 in the reaction with C_2H_6 goes through a sharp maximum with temperature for constant time of retention, and a sharp maximum with time of retention for a given temperature. The experimental determination of the optimum conditions for performing reactions of this type is a delicate and tedious affair, which is complicated by the highly exothermic nature of the reactions and the doubtful significance of observed reaction temperatures.

Since pressure increases the gas-phase concentrations of the reactants, the rates of all reactions involved should be accelerated by the use of pressure; at the same time, it is very unlikely that the dissociation of HNO_3 is apt to be repressed, unless very high pressures are employed. Thus, the possible advantages to be gained by operating under pressure can be ascertained only by careful laboratory investigations and a study of the various economic factors involved.

4. Diolefins. *Illustration 4.*—The diolefin, butadiene, is an important raw material for the manufacture of one type of synthetic rubber. It may be produced by dehydrogenation of 1-butene over chromium, molybdenum, and vanadium oxide catalysts.⁶

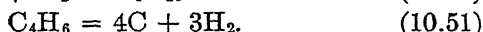
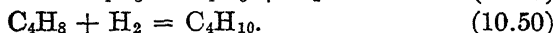
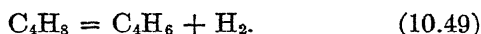
a. Derive an equation for the free-energy change for the formation of butadiene from 1-butene, as a function of temperature, and similar equations for such secondary reactions as appear likely to occur concomitantly with this reaction.

b. Compute the corresponding equilibrium constants at 400°C. and 600°C.

c. Express these equilibrium constants in terms of the fractions of the butene reacted in accordance with the various chemical equations, and compute the equilibrium conversions for the following cases:

| Case | <i>d</i> | <i>e</i> | <i>f</i> |
|---|----------|----------|----------|
| Pressure, atmosphere..... | 1 | 1 | 0.25 |
| Temperature, °C..... | 400 | 600 | 600 |
| Ratio, initial moles inerts to butene.... | 0.05 | 0.05 | 0.05 |

Solution.—*a.* Assume that the external conditions may be controlled so that the following reactions are the only ones occurring to an appreciable extent:



The necessary ΔH_{298} and ΔF°_{298} values have been taken from the review by Thomas, Egloff, and Morrell.⁷

| Compound | ΔH_{298} | ΔF°_{298} |
|--------------------------------------|------------------|------------------------|
| C_4H_6 | 25,770 | 33,960 |
| 1- C_4H_8 | —480 | 16,780 |
| <i>n</i> - C_4H_{10} | —30,570 | —5,000 |

Owing to the large positive free energy of formation of butadiene, any tendency for reaction (10.51) to attain equilibrium would result in the complete decomposition of this compound into carbon and hydrogen; hence it must be assumed that the rate of this reaction is slow compared to the rates at which the first two reactions reach equilibrium.

The free-energy change for reaction (10.49) as a function of temperature may be computed by assuming that the loss of one molecule of H_2 causes a decrease of 2 cal. in the molar-heat capacity of the hydrocarbon, *i.e.*, $\Delta C_p \simeq 5$ for reaction (10.49);

therefore

$$\Delta H = 24,760 + 5.0T, \quad (10.52)$$

$$d\left(\frac{-\Delta F^\circ}{T}\right) = \left(\frac{24,760}{T^2} + \frac{5.0}{T}\right) dT, \quad (10.53)$$

$$-\Delta F^\circ = -24,760 + 11.52T \log T - 3.09T. \quad (10.54)$$

Similarly, for reaction (10.50) it will be assumed that $\Delta C_p = -5.0$; hence

$$\Delta H = -28,600 - 5.0T, \quad (10.55)$$

$$-\Delta F^\circ = 28,600 - 11.52T \log T + 5.64T. \quad (10.56)$$

b. Let $K_1 = \frac{P_{H_2} \cdot P_{C_4H_6}}{P_{C_4H_8}}$, and $K_2 = \frac{P_{C_4H_{10}}}{P_{H_2} \cdot P_{C_4H_8}}$; then, at 400°C ., K_1 and K_2 may be computed from (10.54) and (10.56).

$$K_1 = 2.69 \times 10^{-2} \quad K_2 = 2.34 \times 10^3.$$

At 600°C .,

$$K_1 = 3.43 \quad K_2 = 9.64.$$

c. The reaction system is assumed to be a flow system, operating at constant pressure P . Let n_0 and n_i represent the pound moles of 1-butene and inerts, respectively, entering the converter per hour; and n_H the pound moles of H_2 produced per hour by destructive cracking alone when the system has attained equilibrium with respect to reactions (10.49) and (10.50).

If x = the fraction of C_4H_8 decomposed into butadiene,

y = the fraction of C_4H_8 hydrogenated to C_4H_{10} , and

f = the fraction of original stock cracked completely to carbon and H_2 ,

then, at equilibrium,

$$\text{Moles } C_4H_8 = n_0(1 - x - y - f)$$

$$\text{Moles } C_4H_6 = n_0x$$

$$\text{Moles } C_4H_{10} = n_0y$$

$$\text{Moles } H_2 = 4n_0f + n_0x - n_0y = n_0(4f + x - y)$$

$$\text{Total moles} = n_0(1 + x - y + 3f) + n_i.$$

Therefore

$$P_{C_4H_8} = \frac{(1 - x - y - f)P}{1 + x - y + 3f + r_0}, \quad (10.57)$$

where $r = n_i/n_0$.

Similar expressions may readily be derived for the partial pressures of the other components, which lead to the following

equations for K_1 and K_2 :

$$K_1 = \frac{(4f + x - y)xP}{(1 - x - y - f)(1 + x - y + 3f + r_0)}, \quad (10.58)$$

$$K_2 = \frac{(1 + x - y + 3f + r_0)y}{(1 - x - y - f)(4f + x - y)P}. \quad (10.59)$$

d. $P = 1$ atm., $T = 400^\circ\text{C.}$, $r_0 = 0.05$. Assuming that the fraction of the original stock, irreversibly cracked to C and H_2 , equals 0.01, and substituting in (10.58) and (10.59) give

$$\frac{(0.04 + x - y)x}{(1 - x - y - 0.01)(1 + x - y + 0.08)} = 2.69 \times 10^{-2},$$

$$\frac{(1 + x - y + 0.08)y}{(1 - x - y - 0.01)(0.04 + x - y)} = 2.34 \times 10^3.$$

Unless a great many data are required, the simplest procedure is to solve these equations by trial and error. In this case, $x = 0.445$ and $y = 0.482$. Thus, for the assumed conditions in which only 1 per cent of the butene is completely decomposed, 93 per cent of the butene will react to form butadiene and butane in roughly equimolar proportions.

e. $P = 1$ atm., $T = 600^\circ\text{C.}$, $r_0 = 0.05$. Assuming 2 per cent of the original stock irreversibly cracked to C + H_2 , and substituting in (10.58) and (10.59) give

$$\frac{(0.08 + x - y)x}{(0.98 - x - y)(1.11 + x - y)} = 3.43,$$

$$\frac{(1.11 + x - y)y}{(0.98 - x - y)(0.08 + x - y)} = 9.64.$$

By trial and error, $x = 0.68$ and $y = 0.23$; consequently, temperature favors butadiene formation, but not butane formation.

f. $P = 0.25$ atm., $T = 600^\circ\text{C.}$, $r_0 = 0.05$. Assuming, as previously, that $f = 0.02$, and substituting in (10.58) and (10.59) give

$$\frac{(0.08 + x - y)x}{(0.98 - x - y)(1.11 + x - y)} = 13.72,$$

$$\frac{(1.11 + x - y)y}{(0.98 - x - y)(0.08 + x - y)} = 2.41.$$

Solving these equations as before gives $x = 0.905$ and $y = 0.04$; in other words, 90.5 per cent of the entering butene would be

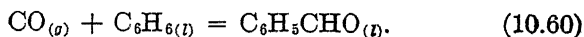
cracked to butadiene, and only 4 per cent would be hydrogenated to butane. Thus, from the equilibrium standpoint, high temperatures and low pressures favor the formation of butadiene.

The optimum conditions of temperature and pressure will be determined by kinetic and specific catalytic factors, which can be predicted in advance only in a qualitative way. Thus, since the rates of all reactions increase with temperature but the formation of butane is disfavored by temperature, it would appear that the higher the temperature of operation, the better the conversion to butadiene. Actually, owing to the greater degree of thermal instability of butadiene, it is to be expected that the lower the temperature, the smaller the destructive cracking of this compound into carbon and H_2 . Consequently an economic balance must be struck between these two opposing factors in order to obtain a maximum economy of conversion to butadiene. Furthermore, since the rate of cracking of the butadiene increases with its concentration, low conversions per pass through the converter will probably result in a greater over-all conversion of the butene to butadiene. One fact, however, does appear quite certain, namely, that low-pressure operation is to be preferred to atmospheric or super-atmospheric pressure operation since the tendency toward butane formation, as well as the polymerization of the butene, is thereby reduced.

5. Benzaldehyde from Carbon Monoxide and Benzene.

Illustration 5.—Estimate a range of conditions of temperature and pressure likely to give practical yields of benzaldehyde, in the reaction between CO and liquid benzene.

Solution.—The reaction to be investigated is



The following thermal data are required:

| Compound | S°_{298} | ΔH_{298} , form. |
|-------------------|-----------------|--------------------------|
| $CO_{(g)}$ | 47.32 | -26,390 |
| $C_6H_{6(l)}$ | 41.9 | 12,870 |
| $C_6H_5CHO_{(l)}$ | 49.4* | -21,860 |

* Estimated.

The entropy of benzaldehyde has been estimated in accordance with the discussion given in Sec. 2, Chap. VIII; the entropies of

CO and C_6H_6 are also recorded in this chapter. The ΔH of formation of benzene is based on the heat of combustion selected by Parks and Huffman, in conjunction with the new heat of formation of CO_2 ; the heat of formation of benzaldehyde is based on the heat of combustion given by Kharasch.⁸

The following free-energy equation is readily derived for reaction (10.60), on the assumption that $\Delta C_p = +5$ cal.:

$$\begin{aligned}\Delta H_{298} &= -8,340 \text{ cal.} & \Delta F^\circ_{298} &= 3,530 \text{ cal.} \\ \Delta H &= -9,830 + 5T, \\ \Delta F^\circ &= -9,830 - 11.52T \log T + 73.5T.\end{aligned}$$

With the standard states as indicated by Eq. (10.60), the equilibrium constant for this reaction is

$$K = \frac{1}{f_{co}} \left(\frac{a_A}{a_B} \right), \quad (10.61)$$

where f_{co} = fugacity of the CO,

a_A = activity of benzaldehyde in solution in C_6H_6 ,

a_B = activity of benzene in solution with the aldehyde.

The equilibrium constant has the value 2.59×10^{-3} at $25^\circ C.$, and therefore the reaction does not look very promising. Since it is exothermic, elevated temperatures do not favor this reaction. The reaction is, however, accompanied by a decrease in volume, and therefore elevated pressures will drive it to the right.

If p_A and p_B are the vapor pressures of pure liquid aldehyde and benzene at 1 atm. pressure (standard reference state), then the free-energy change, corresponding to the transfer of 1 mole of either substance to the total pressure P , is

$$\Delta F_a = RT \ln \frac{f_A^\circ}{p_A} \quad (10.62)$$

and

$$\Delta F_b = RT \ln \frac{f_B^\circ}{p_B}, \quad (10.63)$$

where the f° 's represent the fugacities of the pure liquids at the pressure P . If the solution of aldehyde in benzene under the pressure P is assumed to be ideal,

$$f_A = f_A^\circ N_A \quad \text{and} \quad f_B = f_B^\circ (1 - N_A), \quad (10.64)$$

where N_A is the mole fraction of aldehyde in solution at equilibrium with respect to reaction (10.60), at the total pressure P . Thus the transfer of 1 mole of aldehyde from pure liquid under its own vapor pressure to the equilibrium solution at the pressure P involves the total free-energy change

$$\Delta F_A = RT \ln \frac{f_A^\circ}{p_A} + RT \ln \frac{f_A^\circ N_A}{f_A^\circ} = RT \ln \frac{f_A^\circ N_A}{p_A}. \quad (10.65)$$

Since $\Delta F_A = RT \ln a_A$, the activity of the aldehyde in the equilibrium system is obviously

$$a_A = \frac{f_A^\circ N_A}{p_A}; \quad (10.66)$$

and, similarly, the activity of the benzene in solution is

$$a_B = \frac{f_B^\circ (1 - N_A)}{p_B}. \quad (10.67)$$

The equilibrium constant is, therefore,

$$K = \frac{1}{f_\infty} \frac{f_A^\circ}{f_B^\circ} \frac{p_B}{p_A} \left(\frac{N_A}{1 - N_A} \right); \quad (10.68)$$

and solving for N_A yields

$$N_A = \frac{C}{1 + C}, \quad (10.69)$$

where

$$C = \frac{f_\infty f_B^\circ p_A K}{f_A^\circ p_B} \quad (10.70)$$

and $100N_A$ represents the mole per cent benzene converted to aldehyde.

At 100°C., $\Delta F = 6,500$ cal.; therefore $K = 1.55 \times 10^{-4}$.

The fugacity of the CO at 100 and 500 atm. may be obtained from Fig. 3, Chap. V, and from the critical constants, $T_c = 132.98^\circ\text{K.}$ and $P_c = 34.53$ atm. The fugacities of the pure liquids under pressure may be computed from Eq. (5.16) and the molar volumes and vapor pressures recorded in the table on page 230.

By neglecting the decrease in volume of liquid benzene and benzaldehyde under pressure and assuming the above vapor pressures equal to the fugacities, the fugacities under pressure

were computed from the integral of (5.16) in the form

$$\log \frac{f^\circ}{p} = \frac{V_m}{189T} (P - p), \quad (10.71)$$

where V_m is the molar volume of either liquid.

| Compound | Temperature, °C. | Vapor pressure, 1 atm. | Total pressure, atm. | Molar volume, cc. | Fugacity |
|-------------------|------------------|------------------------|----------------------|-------------------|----------|
| Benzene. | 25 | 0.125 | 100 | 89.5 | 0.179 |
| | 100 | 1.753 | 500 | 98.8 | 8.77 |
| Benzaldehyde..... | 25 | 0.0010 | 100 | 102 | 0.00151 |
| | 100 | 0.0796 | 500 | 109 | 0.470 |
| CO..... | 25 | | 100 | | 97 |
| | 100 | | 500 | | 625 |

At 25°C. and 100 atm.

$$C = \frac{f_{\infty} f_B^\circ p_A K}{f_A^\circ p_B} = \frac{(97)(0.179)(0.001)(2.59 \times 10^{-3})}{(0.00151)(0.125)}$$

$$C = 0.238;$$

therefore

$$N_A = \frac{0.238}{1.238} = 0.192.$$

At 100°C. and 500 atm.

$$C = \frac{(625)(8.77)(0.0796)(1.55 \times 10^{-4})}{(0.470)(1.753)} = 0.082;$$

therefore

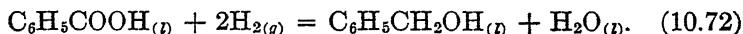
$$N_A = \frac{0.082}{1.082} = 0.0756.$$

Examination of the foregoing figures shows that, at 25° and 100 atm. CO pressure, 19 mole per cent of the benzene is converted to aldehyde at equilibrium in a static system; whereas only 7.6 per cent would be converted at 100°C. and 498 atm. of CO. Thus the reaction does not look very promising unless it can be made to take place at a practical rate, at temperatures below 100°C. and pressures of the order of 500 atm. The experimental evidence indicates that this is unlikely in the absence of a participating catalyst, such as aluminum chloride.

6. Electrolytic Reduction of Benzoic Acid to Benzyl Alcohol.

Illustration 6.—Benzyl alcohol may be produced by cathodic reduction of benzoic acid in aqueous solution. Estimate the electrical energy required to produce one ton of benzyl alcohol by this method.

Solution.—The minimum energy required to reduce benzoic acid to benzyl alcohol may be computed from the free energies of the substances taking part in the reaction

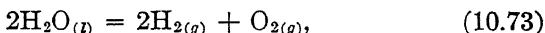


The required values are

$$\begin{aligned} \text{C}_6\text{H}_5\text{COOH}_{(l)}: \Delta F^\circ_{298} &= -59,160 \text{ cal.}, \\ \text{C}_6\text{H}_5\text{CH}_2\text{OH}_{(l)}: \Delta F^\circ_{298} &= -5,230 \text{ cal.}, \\ \text{H}_2\text{O}_{(l)}: \Delta F^\circ_{298} &= -56,694 \text{ cal.}, \end{aligned}$$

where the Parks and Huffman value for benzoic acid has been used, and the ΔF of benzyl alcohol has been based on 894,300 cal. for the heat of combustion and 51.8 for the entropy of this compound. The free-energy change for reaction (10.72) at 25°C. is, therefore, -2,760 cal. and zero at about 80°C. Thus, for all practical purposes the energy requirement for the reaction, as written, is negligible.

However, in order to produce two moles of hydrogen, the process expressed by the equation



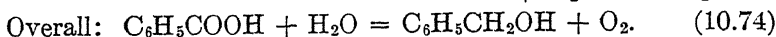
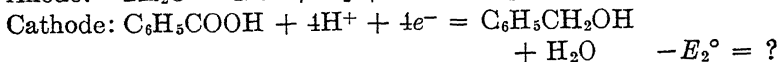
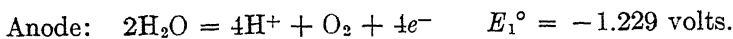
must also take place. Since the free-energy change for this reaction is +113,390 cal., this represents the minimum energy requirement per mole of benzyl alcohol, when the reduction is performed in accordance with Eq. (10.72). The minimum number of kilowatt-hours per ton of benzyl alcohol is, therefore,

$$\text{kilowatt-hours} = \frac{2,000 \times 454 \times 113,390 \times 4.185}{108 \times 3.6 \times 10^6} = 1.11 \times 10^3.$$

With a reasonable price for electrical energy per kilowatt-hour, the above minimum energy requirement does not appear to be excessive.

It is possible to arrive at a more significant value for the energy requirements by visualizing a reasonable type of cell in which the reduction process might be carried out. Consider a

cell consisting of a porous cylinder for a cathode compartment, situated inside a larger cylinder serving as anode compartment. The anode compartment contains an aqueous solution of sulphuric acid, and the cathode compartment contains the same electrolyte, plus benzoic acid. The electrodes might be made of sheet lead. The passage of 4 faradays of electricity through this cell under reversible conditions effects the following changes of state:



An estimate for E_2° may be obtained as follows: Parks and Huffman give $-57,950$ cal. for the free energy of formation of $\text{C}_6\text{H}_5\text{COOH}_{(aq)}$; if the solubility of benzyl alcohol in water at 25°C . is estimated to be of the order of 0.5 molal, the free energy of formation of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}_{(aq)}$ is approximately

$$\Delta F^\circ_{298} = -5,230 + 1,364 \log \frac{1}{0.5} = -4,820 \text{ cal.}$$

Even if the estimated solubility of the alcohol is in error by a factor of 10, the effect on the final answer will be entirely negligible. Accordingly, the standard free-energy change for the cathode reaction is

$$\Delta F^\circ_{298} = -56,694 - 4,820 + 57,950 = -3,564 \text{ cal.,}$$

and

$$-E_2^\circ = \frac{3,564}{4(23,066)} = 0.0386 \text{ volt.}$$

Consequently, the standard reversible electromotive force for the visualized cell, in which reaction (10.74) takes place, is approximately

$$E^\circ = E_1^\circ - E_2^\circ = -1.229 + 0.039 = -1.19 \text{ volts.}$$

The reversible electromotive force of this cell corresponding to actual concentrations or activities is, therefore,

$$E = E_1^\circ - \frac{RT}{4F} \ln \frac{(\text{H}^+)^4 P_{\text{O}_2}}{(\text{H}_2\text{O})^2} - \left[E_2^\circ - \frac{RT}{4F} \ln \frac{(\text{HBz})(\text{H}^+)^4}{(\text{BzOH})(\text{H}_2\text{O})} \right]$$

or

$$E = -1.19 - 0.0147 \log \frac{P_{O_2}(\text{BzOH})}{(\text{H}_2\text{O})(\text{HBz})}. \quad (10.75)$$

If the concentration of H_2SO_4 is not too large, the ratio $(\text{BzOH})/(\text{HBz})$ is substantially the same as in pure water, and the activity of the H_2O is close to unity; therefore

$$E_{298} = -1.19 - 0.0147 \log \frac{(1)(0.5)}{(1)(0.0279)} \simeq -1.208,$$

when $P_{O_2} = 1.0$ atm. Furthermore, it should be noted that, even if it were possible to alter P_{O_2} and the activities appearing in the log term such that the factor

$$\frac{P_{O_2}(\text{BzOH})}{(\text{H}_2\text{O})(\text{HBz})},$$

varied by as much as 10^6 , the over-all electromotive forces would change only by -0.0882 volt. Thus it must be concluded that the reversible electromotive force of this cell is not particularly dependent on concentration changes.

The total actual electromotive force of the cell in operation is the sum of the reversible electromotive force, the IR drop through the cell, and the overvoltages at the two electrodes corresponding to the current density employed to give practical rates of reduction. Now the IR drop depends on the total current through the cell (I) and the total resistance of the cell (R). Since this latter factor depends to such a large extent on the composition of the electrolyte, temperature, shape, and size of electrodes, as well as their relative disposition, no attempt will be made to compute this quantity. A reasonable IR drop for a commercial cell is 1 to 2 volts, and therefore 1.5 volts will be assumed in this case.

With a current density of 0.1 amp./sq. cm., the hydrogen overvoltage at a lead electrode in one molal H_2SO_4 is known to be 1.18 volts at 25°C . This should represent a reasonable upper limit for the cathode overvoltage in the reduction of benzoic acid; since, if this value were exceeded, H_2 would be discharged as such, instead of being captured by the carboxyl group. No data are available for the oxygen overvoltage at a lead electrode in sulphuric acid, but the same value will be assumed. The

operating electromotive force of this cell at 25°C. is estimated to be

$$E = 1.208 + 1.5 + 2(1.18) = 5.06 \text{ volts.}$$

In the actual reduction some H_2 is likely to escape from the cathode compartment, and certain undesirable secondary cell reactions might also occur; consequently an over-all current efficiency of 80 per cent will be assumed. That is, instead of requiring four faradays to produce 1 mole of the alcohol, 5 faradays will be required. The energy expended in the production of 1 g. mole is, therefore,

$$5(96,494)(5.06) = 24.4 \times 10^5 \text{ joules}$$

or, per ton of benzyl alcohol,

$$\text{kilowatt-hours} = \frac{2,000 \times 454 \times 24.4 \times 10^5}{108 \times 3.6 \times 10^6} = 5.7 \times 10^3.$$

Thus it will be seen that the actual energy requirement, corresponding to the cell reaction expressed by Eq. (10.74), is about five times as great as the minimum requirement, corresponding to the reaction expressed by Eq. (10.72). The cost of electrical energy for such a reduction process might therefore appear to be prohibitive, unless unusually cheap power were available.

No mention has been made of the possibility of favorably influencing the efficiency of the reduction by altering the temperature of operation or the electrolyte concentration. In view of the low solubility of benzoic acid in water at ordinary temperatures, the rate of reaction between H_2 and the acid at the cathode would be slow, and considerable H_2 would escape from the cathode. Increasing the temperature of operation and the H_2SO_4 concentration of the electrolyte would probably improve these kinetic factors, but would increase the reversible electromotive force of the cell. However, since elevated temperatures usually decrease the overvoltage, the net result of higher temperatures would probably be favorable. In fact, it is probably necessary to operate at elevated temperatures if a current efficiency of 80 per cent is to be realized.

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CHAPTER XI

FLAME TEMPERATURES

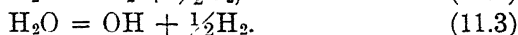
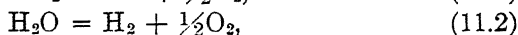
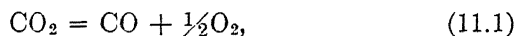
Theoretical flame temperatures are of importance in engineering considerations (1) because they represent the maximum possible temperatures or potentials at which the thermal energy, produced by a given combustion process, will be available for conversion to work; and (2) because the magnitude of the temperature determines to a considerable extent the materials of construction to be employed for fabricating the combustion apparatus. In spite of the fact that calculations of flame temperatures are based on the assumption that the process is adiabatic, the results so obtained usually agree with actual flame temperatures within about 100°C. The calculations are complicated by the fact that the temperatures ultimately attained under adiabatic conditions may be high enough to dissociate the CO_2 and H_2O . In this case the final equilibrium system contains CO_2 , H_2O , CO , O_2 , H_2 , and OH molecules, in addition to inerts present in the original gas mixture. Since the extent of dissociation depends on the final temperature—and this in turn depends on the total heat liberated, which is also determined by the dissociation—it is obvious that the problem is quite involved.

1. Theoretical Flame Temperature in Combustion of Propane.

Illustration.—A mixture of propane and air is to be burned, using the stoichiometric quantity of air. Compute the theoretical flame temperature for this process, assuming the reactants initially at 25°C.

Solution.—In the absence of preliminary information to the contrary, it is advisable to assume that the maximum temperature will be high enough for the CO_2 and H_2O formed to be partially dissociated. Accordingly, the correct evaluation of the theoretical temperature requires a knowledge of the equilibria involving the possible species, H_2O , CO_2 , CO , H_2 , O_2 , and OH at the temperature attained by the system.

Since accurate values for the equilibrium constants of the following three reactions are available,¹ these equations will be employed to evaluate the equilibrium conditions at the unknown temperature attained by the system



Let n_1 = total moles of CO_2 stoichiometrically equivalent to complete combustion of 1 mole of the combustible compound (C_3H_8).

n_2 = total moles of H_2O stoichiometrically equivalent to complete combustion of 1 mole of the combustible compound.

x = fraction total moles CO_2 dissociated in accordance with Eq. (11.1).

y = fraction total moles H_2O dissociated in accordance with Eq. (11.2).

z = fraction total moles H_2O dissociated in accordance with Eq. (11.3).

At equilibrium

$$\begin{aligned} \text{moles CO}_2 &= n_1(1 - x) \\ \text{moles CO} &= n_1x \\ \text{moles H}_2\text{O} &= n_2(1 - y - z) \\ \text{moles OH} &= n_2z \\ \text{moles O}_2 &= \frac{n_1x}{2} + \frac{n_2y}{2} \\ \text{moles H}_2 &= \frac{n_2}{2}(2y + z) \end{aligned}$$

and the moles of N_2 present in the air are designated by n . The total moles at equilibrium are given by the expression

$$\sum \text{moles} = n_1 \left(1 + \frac{x}{2}\right) + n_2 \left(1 + \frac{y}{2} + \frac{z}{2}\right) + n. \quad (11.4)$$

Since n is a large number, and the fractional dissociations are quite small, no great error will be introduced if this expression is simplified to

$$\Sigma \text{moles} = n_1 + n_2 + n. \quad (11.5)$$

Consequently,

$$P_{\text{CO}_2} = \frac{n_1(1-x)P}{n_1 + n_2 + n} = \frac{n_1(1-x)P}{\Sigma}$$

$$P_{\text{CO}} = \frac{n_1 x P}{\Sigma}, \text{ etc.}$$

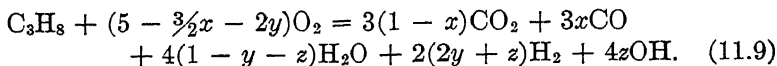
Substituting these partial pressures in the equilibrium equations corresponding to (11.1) to (11.3) gives

$$K_1 = \frac{x}{1-x} \left[(n_1 x + n_2 y) \frac{P}{2\Sigma} \right]^{1/2}, \quad (11.6)$$

$$K_2 = \frac{2y+z}{2(1-y-z)} \left[(n_1 x + n_2 y) \frac{P}{2\Sigma} \right]^{1/2}, \quad (11.7)$$

$$K_3 = \frac{z}{1-y-z} \left\{ [n_2(2y+z)] \frac{P}{2\Sigma} \right\}^{1/2}. \quad (11.8)$$

Equations (11.6) to (11.8) contain three unknowns, but cannot be solved for x , y , and z because the maximum flame temperature is still unknown, and therefore K_1 , K_2 , and K_3 are as yet undetermined. The fourth required relation can be found in the expression for the heat evolved by the combustion reaction as follows: For the combustion of propane $n_1 = 3$ and $n_2 = 4$; therefore the net effect of the adiabatic reaction per mole of C_3H_8 is



[All substances in Eq. (11.9) are in the gaseous state.] Since the heats of formation and heat capacities of all the species involved in this reaction are known, a system of four equations involving the four unknowns x , y , z , and T can be set up, which permits a definite solution of the problem. Unfortunately, an explicit solution of this system of equations for the four unknowns is not possible; therefore, a tedious trial-and-error method must be employed.

In using Eq. (11.9), two different procedures are possible. It can be assumed that the initial mixture of propane and air is heated up to the unknown temperature T , and there permitted to react to equilibrium, in accordance with (11.9); or it can be assumed that the reaction occurs at 25°C . to the extent permitted by the equilibrium conditions at the temperature T , and this

mixture of gases is then heated up to the temperature T . Since the energy in excess of the zero-point energy of all these gases, except propane, is available in tabulations² and is given in Table 1 below, it is obvious that the second procedure is preferable. Values of energy contents recorded in Table 1 are for the ideal gas state, and may be readily converted to enthalpies by the addition of $1.987T$.

TABLE 1.—THE ENERGY CONTENT $\left(\int_0^T C_p dT\right)$ OF GASES IN CALORIES PER MOLE*

| Temp., °K. | Gas | | | | | | | | | | |
|---------------|----------------|----------------|----------------|--------|--------|--------|-----------------|------------------|----------------|-----------------|-------|
| | H ₂ | O ₂ | N ₂ | CO | NO | OH | CO ₂ | H ₂ O | O ₃ | Br ₂ | HBr |
| 200 | 965 | 995 | 992 | 992 | 1,095 | | | 1,192 | 1,229 | 1,134 | 994 |
| 250 | 1,197 | | | | | | | | | 1,454 | 1,243 |
| 300 | 1,440 | 1,492 | 1,489 | 1,489 | 1,616 | 1,523 | 1,660 | 1,791 | 1,950 | 1,783 | 1,493 |
| 400 | 1,936 | 2,004 | 1,987 | 1,989 | 2,132 | 2,034 | 2,403 | 2,409 | 2,786 | 2,456 | 1,991 |
| 500 | | | | | | | | | 3,660 | 3,140 | 2,493 |
| 600 | 2,936 | 3,086 | 3,006 | 3,017 | 3,196 | 3,048 | 4,135 | 3,687 | 4,627 | 3,830 | 3,003 |
| 700 | | | | | | | | | 5,644 | 4,524 | 3,525 |
| 800 | 3,947 | 4,262 | 4,080 | 4,112 | 4,332 | 4,069 | 6,107 | 5,073 | 6,702 | 5,222 | 4,061 |
| 900 | | | | | | | | | 7,793 | 5,923 | 4,612 |
| 1000 | 4,979 | 5,509 | 5,217 | 5,271 | 5,534 | 5,118 | 8,246 | 6,577 | 8,909 | 6,626 | 5,179 |
| 1200 | 6,044 | 6,814 | 6,442 | 6,487 | 6,786 | 6,200 | 10,500 | 8,200 | | 8,037 | 6,355 |
| 1400 | 7,155 | 8,150 | 7,659 | 7,749 | 8,074 | 7,330 | 12,840 | 9,920 | | 9,455 | 7,579 |
| 1600 | 8,295 | 9,514 | 8,920 | 9,045 | 9,389 | 8,525 | 15,220 | 11,750 | | 10,880 | 8,843 |
| 1800 | 9,478 | 10,920 | 10,220 | 10,355 | 10,724 | 9,740 | 17,680 | 13,670 | | | |
| 2000 | 10,702 | 12,352 | 11,533 | 11,670 | 12,075 | 10,990 | 20,180 | 15,650 | | | |
| 2200 | 11,945 | 13,815 | 12,860 | 13,007 | 13,439 | 12,255 | 22,680 | 17,710 | | | |
| 2400 | 13,233 | 15,314 | 14,199 | 14,354 | 14,814 | 13,565 | 25,240 | 19,780 | | | |
| 2600 | 14,554 | 16,825 | 15,554 | 15,732 | 16,197 | 14,890 | 27,830 | 21,930 | | | |
| 2800 | 15,894 | 18,350 | 16,926 | 17,110 | 17,588 | 16,250 | 30,450 | 24,150 | | | |
| 3000 | 17,234 | 19,887 | 18,295 | 18,484 | 18,985 | 17,607 | 33,000 | 26,330 | | | |
| 3200 | 18,586 | 21,415 | 19,672 | 19,923 | 20,387 | 19,000 | | | | | |
| 3500 | 20,654 | 23,700 | 21,747 | 21,951 | 22,500 | 21,105 | | | | | |

* Prepared by Lewis and Von Elbe, *J. Am. Chem. Soc.*, **57**, 612 (1935).

The following values have been employed for heats of formation in these calculations:

| Compound | $-\Delta H_{298}$, cal. per mole |
|-------------------------------|-----------------------------------|
| C ₃ H ₈ | 24,790 |
| CO ₂ | 94,030 |
| CO | 26,394 |
| H ₂ O | 57,800 |
| OH | 5,930 |

The heat liberated by reaction (11.9) is given by the equation

$$\Delta H_{298} = -23,720z - 231,200(1 - y - z) - 79,180x \\ - 282,090(1 - x) + 24,790. \quad (11.10)$$

This heat evolution may then be equated to the sum of the enthalpies of the products, plus excess O_2 (if any), plus N_2 between 298.1°K. and $T^\circ K$.

If the mole of propane is burned with the stoichiometric amount of air, then a total of (1) (5) (100/21) = 23.8 moles of air are required. The products of combustion will then contain 18.8 moles of $N_2(n)$.

The total enthalpy of the products is, therefore,

$$\Sigma H^r_{298} = 18.8H_{N_2} + (1.5x + 2y)H_{O_2} + 3(1 - x)H_{CO_2} + 3xH_{CO} \\ + 4(1 - y - z)H_{H_2O} + 2(2y + z)H_{H_2} + 4zH_{OH} \quad (11.11)$$

and is equal to $-\Delta H_{298}$ computed from Eq. (11.10).

In order to apply Eq. (11.11), some convenient simplifications may be performed without introducing appreciable errors. In the first place the total energy content of the products as read from Table 1 may be converted to heat content by the addition of the term ΣRT . Since Σ is very nearly 25.8 moles, it follows that

$$\Sigma H^r_{298} = \Sigma E^r_{298} + 51.26(T - 298). \quad (11.12)$$

In the second place, a glance at Table 1 shows that the energy contents of H_2 and OH are roughly equal; and, since they constitute but a small portion of the total energy content of the system, it is permissible to treat the OH as if it were H_2 . Again, since the energy content of the CO is almost equal to that of the N_2 , and since it is present in relatively small amounts, it can be treated as if it were nitrogen. With these simplifications Eq. (11.12) becomes

$$\Sigma H^r_{298} = (18.8 + 3x)E_{N_2} + (1.5x + 2y)E_{O_2} + 3(1 - x)E_{CO_2} \\ + 4(1 - y - z)E_{H_2O} + 2(2y + 3z)E_{H_2} \\ + 51.26(T - 298). \quad (11.13)$$

It should be noted that the energy contents to be substituted in this equation are the values read from Table 1 at the temperature T , minus the energy contents at 298°K. With the help of the numerical values of the equilibrium constants plotted on Fig. 14,

Eqs. (11.6), (11.7), (11.8), (11.10), and (11.13) may now be solved for x , y , z , and T by trial and error.

Assuming that $T = 2250^\circ\text{K.}$ and $P = 1$ atm., then $K_1 = 8.8 \cdot 10^{-3}$, $K_2 = 1.68 \cdot 10^{-3}$, $K_3 = 2.53 \cdot 10^{-3}$ (Fig. 14), and Eqs. (11.6) to (11.8) become

$$\begin{aligned}\frac{x}{1-x} (3x + 4y)^{1/2} &= 6.32 \cdot 10^{-2}. \\ \frac{2y + z}{2(1-y-z)} (3x + 4y)^{1/2} &= 1.21 \cdot 10^{-2}. \\ \frac{z}{1-y-z} [4(2y + z)]^{1/2} &= 1.82 \cdot 10^{-2}.\end{aligned}$$

Guess $x = 0.10$; $y = 0.006$; $z = 0.04$.

$$\begin{aligned}\frac{0.10}{0.90} (0.30 + 0.024)^{1/2} &= 6.34 \cdot 10^{-2}. \\ \frac{0.026}{0.954} (0.30 + 0.024)^{1/2} &= 1.55 \cdot 10^{-2}. \\ \frac{0.04}{0.954} (0.208)^{1/2} &= 1.91 \cdot 10^{-2}.\end{aligned}$$

Substituting these values of x , y , and z in Eq. (11.10) gives

$$\begin{aligned}\Delta H_{298} &= -23,270(0.04) - 231,200(0.954) - 79,180(0.10) \\ &\quad - 282,090(0.90) + 24,790, \\ -\Delta H_{298} &= 458,080.\end{aligned}$$

ΣE^T_{298} may now be computed from Eq. (11.13) by substituting the above values for x , y , and z and values for E^T_{298} read from Table 1. Thus,

$$\begin{aligned}\Sigma E^{2250}_{298} &= 19.1(11,716) + (0.162)(12,712) + 2.70(21,676) \\ &\quad + 3.82(16,453) + 0.264(10,841), \\ \Sigma E^{2250}_{298} &= 350,330,\end{aligned}$$

or

$$\Sigma H^{2250}_{298} = 350,330 + 115,200 - 15,250 = 450,280 \text{ cal.}$$

It will be noticed that the computed heat liberation is equivalent to an increase in enthalpy of 458,080 cal., whereas the heat content of the products of combustion between 298 and 2250°K. is 450,280 cal. Thus the heat liberated by the combustion is about 1.7 per cent more than that required to raise the products

of combustion from 25 to 1977°C. If an extremely accurate value for the flame temperature were required, it would be necessary to repeat these calculations, assuming a temperature about 20° higher, and solving for new and larger values of x , y , and z at the higher temperature. As it is, it would probably be

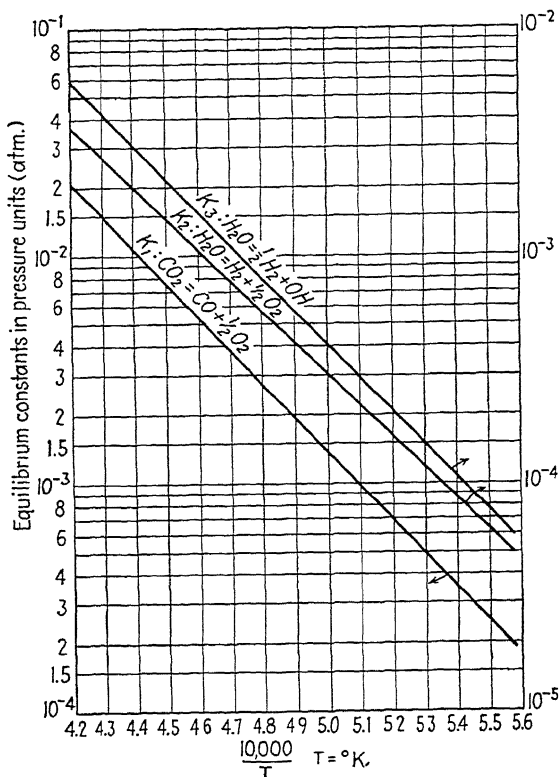


FIG. 14.—Equilibrium constants used in flame-temperature calculations.

sufficiently accurate to raise the total temperature rise of 1952° by 1.7/2 per cent, giving an adjusted temperature rise of 1969°. This is equal to a theoretical flame temperature of 1994°C. for the combustion of 1 mole of C_3H_8 with the stoichiometric amount of air.

References

1. LEWIS and VON ELBE: "Combustion, Flames, and Explosions of Gases," The Macmillan Company, New York, 1938.
2. LEWIS and VON ELBE: *J. Am. Chem. Soc.*, **57**, 612 (1935).

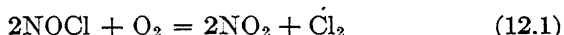
CHAPTER XII

CONVERTER DESIGN

1. General Considerations.—The design of a suitable vessel for carrying out a reaction in a continuous manner may frequently be facilitated when data in the literature concerning the thermochemical and kinetic properties of the reaction in question are properly utilized. In spite of the fact that most industrially important reactions are performed in the presence of catalysts, data on homogeneous, noncatalytic reactions are of value in affording preliminary estimates of the size and weight of the reaction vessel required to perform a given reaction. Although estimates so obtained are upper limits, they are of definite value for preliminary cost estimating and in rating the economic merits of catalysts developed in the laboratory.

The thermochemical characteristics of the reaction enter the considerations in that reactions become infinitely slow as equilibrium is approached, thereby requiring an unduly large reactor or, owing to large heat effects (positive or negative) accompanying the reaction, it is necessary to arrange the converter parts so as to add or subtract heat from the reaction mass. This is essential in order to control temperatures within certain limits. The method of attacking such problems is illustrated by the two illustrations presented in this chapter. In the first illustration the reaction is mildly exothermic so that kinetic and equilibrium factors are of principal importance; in the second case, enthalpy changes accompanying the reaction are of equal importance with kinetic factors.

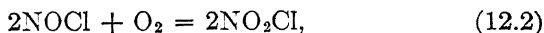
The oxidation of nitrosyl chloride with air or oxygen offers a possible method for separating this compound into chlorine and nitrogen dioxide. The gas-phase reaction



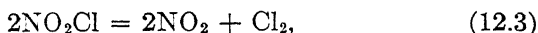
might be expected to proceed more rapidly with increasing temperature, but, since the reaction is exothermic, the equilibrium is shifted to the left with increasing temperature. Furthermore,

since the reaction, as written, involves no volume change other than the association of NO_2 to N_2O_4 at low temperatures, the equilibrium is not appreciably altered by pressure changes.

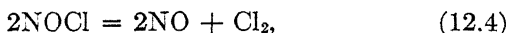
In the absence of definite experimental information regarding the mechanism of the homogeneous reaction, it is difficult to estimate the magnitude of the effect of increased pressures on the rate of the reaction. If the mechanism of the oxidation involved the intermediate formation of nitryl chloride, thus,



followed by



and, if reaction (12.2) were the rate-controlling step, the rate would be expected to increase rapidly with pressure due to the increasing concentrations of the reactants and the fact that the rate is a function of the third power of the concentrations. However, since Schumacher and Sprenger¹ have measured the rate of decomposition of NO_2Cl at 100°C ., it does not seem reasonable to postulate the primary formation of this compound at still higher temperatures. An alternative mechanism which presents no such obvious objections is offered by the following set of simultaneous reactions:

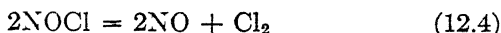


This mechanism has the additional advantage that reliable data are available on the rate constants of the two pairs of opposing reactions; consequently, it is possible to discuss, in an approximately quantitative way, the effect of temperature, concentrations, and pressure on the rate of the over-all oxidation reaction (12.1), in advance of actual experimental data. Such calculations may be of considerable assistance in deciding upon the most economical conditions of pressure and temperature under which to operate and the economics of the use of O_2 vs. air for oxidation. The procedure is discussed in illustration 1.

2. Estimation of Converter Size in the Oxidation of NOCl .

Illustration 1.—Estimate the size of converter required to oxidize NOCl with air at 300°C . and 5 atm., to within 80 per cent of the equilibrium value. The nitrosyl chloride is to be fed to the converter at the rate of 1 pound mole/(hr.)(sq. ft.) of converter cross section.

Solution.—The reactions



are assumed to take place simultaneously and independently of each other with specific reaction velocities equal to those determined for the two separate reactions. The reaction rate constants for the NOCl decomposition and formation given by Welinsky and Taylor² will be used, and the Bodenstein³ constants will be employed for the rate of NO oxidation. At 300°C., these authors give the following values for the required rate constants:

$$k_1 \text{ (NOCl decomposition)} = 10.1 \cdot 10^3, \text{ cc./ (mole)(sec.)}$$

$$k_1' \text{ (NOCl formation)} = 25.3 \cdot 10^8, \text{ cc.}^2\text{/ (mole}^2\text{)(sec.)}$$

$$k_2 \text{ (NO}_2\text{ formation)} = 1.13 \cdot 10^4, \text{ l}^2\text{/ (mole equiv.}^2\text{)(sec.)}$$

For computations on a constant-pressure system, these constants are more conveniently employed in pressure units, with time in hours. Substituting

$$(\text{NOCl}) = \frac{P_{\text{NOCl}}}{RT} \quad (12.6)$$

in

$$k_1 = - \frac{1}{(\text{NOCl})^2} \left[\frac{d(\text{NOCl})}{dt} \right], \quad (12.7)$$

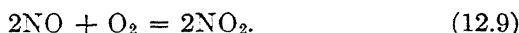
where (NOCl) represents the concentration in moles per cubic centimeter, shows that

$$\frac{dP_{\text{NOCl}}}{dt} = - \frac{k_1}{RT} (P_{\text{NOCl}})^2. \quad (12.8)$$

Thus, in order to convert k_1 in concentration units to atmospheres, it is necessary to divide by RT ; to convert to time in hours, to multiply by 3,600. That is, $(43.9/T)(k_1)$ is the required rate constant in practical units. In a similar manner it may be shown that k_1' divided by $(RT)^2$ equals the rate of formation of NOCl in pressure units, or, in practical units, the constant is $(0.534/T)(k_1')$.

In the case of the Bodenstein oxidation constants, the factor for converting from concentration to pressure units is $1/2R^2T^2$, because the NO concentration is expressed as one-half the moles of NO per liter. The rate constant in practical units is therefore $(2.67 \cdot 10^5/T^2)(k_2)$.

In order to obtain the specific reaction rate for the decomposition of NO_2 , the relation $K = k_2/k_2'$ is employed, where K is the equilibrium constant for the reaction



The equilibrium constant for this reaction at 300°C . may be computed from Giauque and Kemp's⁴ values for the ΔF° 's and ΔH 's of these compounds at 25°C . and the relation

$$d\left(\frac{\Delta F^\circ}{T}\right) = -\frac{\Delta H}{T^2} dT. \quad (12.10)$$

The heat capacities of NO and O_2 are given by Kelley as

$$\text{NO: } C_p = 8.05 + 0.233 \cdot 10^{-3}T - 1.56 \cdot 10^5 T^{-2}, \quad (12.11)$$

$$\text{O}_2: C_p = 8.27 + 0.258 \cdot 10^{-3}T - 1.877 \cdot 10^5 T^{-2}; \quad (12.12)$$

and the following frequencies used by Giauque and Kemp may be employed to compute the heat capacity of NO_2 by the method of Sec. 5, Chap. VII:

$$\omega_1 = 641 \text{ cm.}^{-1}; \quad \omega_2 = 1,373 \text{ cm.}^{-1}; \quad \omega_3 = 1,615 \text{ cm.}^{-1}$$

| | | | | |
|-------------------------------------|------|-------|-------|-------|
| Temperature, $^\circ\text{K}$ | 300 | 500 | 700 | 900 |
| C_p , cal./mole..... | 9.08 | 10.51 | 11.60 | 12.30 |

On the basis of these heat capacities, ΔC_p for reaction (12.9) is small—of the order of -2.0 cal. in the range 25 to 300°C .; consequently,

$$\Delta H = -26,530 - 2.0T \quad (12.13)$$

and

$$\Delta F^\circ = -26,530 + 4.61T \log T + 21.4T. \quad (12.14)$$

At 573°K ., $\log K = 2.65$ and $K = 447$.

The above data are now adequate for computing the rate constants for the four reactions indicated by Eqs. (12.4) and (12.5) at 300°C .

$$k_1 = \frac{10.1 \cdot 10^3(43.9)}{573} = 7.74 \cdot 10^2.$$

$$k_1' = \frac{25.3 \cdot 10^8(0.534)}{573^2} = 4.11 \cdot 10^3.$$

$$k_2 = \frac{1.13 \cdot 10^4(2.67 \cdot 10^5)}{573^2} = 0.916 \cdot 10^4.$$

$$k_2' = \frac{k_2}{K} = \frac{0.916 \cdot 10^4}{0.447 \cdot 10^3} = 20.5.$$

In order to apply these four constants, consider an empty cylindrical reactor of 1 sq. ft. in cross section and of unknown height h , into which 1 lb. mole of NOCl, plus 2.5 lb. moles of air at 5 atm. are fed per hour. The following material balance conditions may be set up for steady conditions of operation:

- (1) Pound moles NOCl leaving converter per hour = pound moles NOCl entering per hour - pound moles NOCl decomposed per hour by (12.4).
- (2) Pound moles O₂ leaving converter per hour = pound moles O₂ entering per hour - pound moles reacted per hour by (12.5).

These conditions are expressed by means of the equations

$$n_n^\circ(1 - x) = n_n^\circ - \int_V \left(- \frac{\partial \text{NOCl}}{\partial t} \right) dt \quad (12.15)$$

$$n_o^\circ(1 - y) = n_o^\circ - \int_V \left(- \frac{\partial \text{O}_2}{\partial t} \right) dt, \quad (12.16)$$

where x represents the fraction of the entering (n_n°) moles of NOCl decomposed, y represents the fraction of the entering (n_o°) moles of O₂ reacted, and the integrals are to be computed over the converter volume V .

Let Σ_0 = pound moles NOCl + O₂ + N₂ entering the converter per hour (assumed constant throughout converter).

P = total pressure in atmospheres.

T = temperature of converter in degrees Kelvin (assumed constant throughout).

Then, if the ideal gas laws are assumed for this gas mixture, the time spent by the gas in the element of converter volume dV is

$$dt = \frac{P dh}{\Sigma_0 R T}. \quad (12.17)$$

Substituting Eq. (12.17) in (12.15) and (12.16) and differentiating yield

$$n_n^\circ \frac{dx}{dh} = \left(- \frac{\partial \text{NOCl}}{\partial t} \right) \frac{P}{\Sigma_0 R T}, \quad (12.18)$$

$$n_o^\circ \frac{dy}{dh} = \left(- \frac{\partial \text{O}_2}{\partial t} \right) \frac{P}{\Sigma_0 R T}. \quad (12.19)$$

The coefficients in parentheses representing the rates of decomposition of NOCl and consumption of O₂ may be evaluated

in terms of the known kinetic equations for reactions (12.4) and (12.5). Thus, according to Welinsky and Taylor, the net rate of decomposition of NOCl is given by the equation

$$-\frac{\partial P_{\text{NOCl}}}{\partial t} = k_1 P_{\text{NOCl}}^2 - k_1' P_{\text{NO}}^2 P_{\text{Cl}_2}, \quad (12.20)$$

and, according to Bodenstein, the net rate of NO oxidation is

$$-\frac{\partial P_{\text{NO}}}{\partial t} = k_2 P_{\text{NO}}^2 P_{\text{O}_2} - k_2' P_{\text{NO}_2}, \quad (12.21)$$

But

$$-\frac{\partial P_{\text{NO}}}{\partial t} = -2 \frac{\partial P_{\text{O}_2}}{\partial t} \quad (12.22)$$

and, therefore,

$$-\frac{\partial P_{\text{O}_2}}{\partial t} = \frac{k_2}{2} P_{\text{NO}}^2 P_{\text{O}_2} - \frac{k_2'}{2} P_{\text{NO}_2}. \quad (12.23)$$

Substituting the following values for the individual partial pressures in Eqs. (12.20) and (12.23)

$$P_{\text{NOCl}} = n_n^\circ (1 - x) \frac{P}{\Sigma_0}, \quad (12.24)$$

$$P_{\text{NO}} = (n_n^\circ x - 2n_0^\circ y) \frac{P}{\Sigma_0}, \quad (12.25)$$

$$P_{\text{Cl}_2} = n_n^\circ x \frac{P}{2\Sigma_0}, \quad (12.26)$$

$$P_{\text{O}_2} = n_0^\circ (1 - y) \frac{P}{\Sigma_0}, \quad (12.27)$$

$$P_{\text{NO}_2} = 2n_0^\circ y \frac{P}{\Sigma_0}, \quad (12.28)$$

gives

$$\begin{aligned} \frac{n_n^\circ P}{\Sigma_0} \frac{\partial x}{\partial t} &= k_1 \left(\frac{n_n^\circ P}{\Sigma_0} \right)^2 (1 - x)^2 \\ &\quad - \frac{k_1' P^3}{2\Sigma_0^3} n_n^\circ (n_n^\circ x - 2n_0^\circ y)^2 x, \end{aligned} \quad (12.29)$$

$$\begin{aligned} \frac{n_0^\circ P}{\Sigma_0} \frac{\partial y}{\partial t} &= \frac{k_2 P^3}{2\Sigma_0^3} n_0^\circ (n_n^\circ x - 2n_0^\circ y)^2 (1 - y) \\ &\quad - 2k_2' \left(\frac{P n_0^\circ}{\Sigma_0} \right)^2 y^2. \end{aligned} \quad (12.30)$$

Since

$$-\frac{\partial \text{NOCl}}{\partial t} = -\frac{\partial n_n^\circ (1 - x)}{\partial t} = n_n^\circ \frac{\partial x}{\partial t} \quad (12.31)$$

and

$$-\frac{\partial O_2}{\partial t} = -\frac{\partial n_0^\circ(1-y)}{\partial t} = n_0^\circ \frac{\partial y}{\partial t}, \quad (12.32)$$

it follows that

$$-\frac{\partial \text{NOCl}}{\partial t} = \frac{k_1(n_n^\circ)^2 P}{\Sigma_0} (1-x)^2 - \frac{k_1' P^2}{2\Sigma_0^2} n_n^\circ (n_n^\circ x - 2n_0^\circ y)^2 x \quad (12.33)$$

and

$$-\frac{\partial O_2}{\partial t} = \frac{k_2 P^2 n_0^\circ}{2\Sigma_0^2} (n_n^\circ x - 2n_0^\circ y)^2 (1-y) - \frac{2k_2' P (n_0^\circ)^2}{\Sigma_0} y^2. \quad (12.34)$$

Let r_0 = ratio moles NOCl to O_2 entering the converter and substitute (12.33) and (12.34) in (12.18) and (12.19), respectively. Then

$$\frac{dx}{dh} = C_1(1-x)^2 - C_2(r_0x - 2y)^2x, \quad (12.35)$$

$$\frac{dy}{dh} = C_3(r_0x - 2y)^2(1-y) - C_4y^2, \quad (12.36)$$

where

$$C_1 = \frac{k_1 P^2 N_n^\circ}{\Sigma_0 R T}, \quad C_2 = \frac{k_1' P^3 (N_0^\circ)^2}{2 \Sigma_0 R T},$$

$$C_3 = \frac{k_2 P^3 (N_0^\circ)^2}{2 \Sigma_0 R T}, \quad C_4 = \frac{2k_2' P^2 N_0^\circ}{\Sigma_0 R T},$$

and N_n° and N_0° are the inlet mole fractions of NOCl and O_2 , respectively.

The equilibrium x and y corresponding to any set of operating conditions may be computed from (12.35) and (12.36) by noting that, at equilibrium,

$$\frac{dx}{dh} = \frac{dy}{dh} = 0; \quad (12.37)$$

consequently, Eqs. (12.35) and (12.36) simplify to

$$\frac{C_1}{C_2} = \frac{(r_0x - 2y)^2x}{(1-x)^2} \quad (12.38)$$

and

$$\frac{C_3}{C_4} = \frac{y^2}{(r_0x - 2y)^2(1-y)} \quad (12.39)$$

Equations (12.38) and (12.39) may be solved for x and y by trial and error when the constants corresponding to the given conditions have been computed. The necessary rate constants are given above and, in addition, $\Sigma_0 = 3.5$, $P = 5 \text{ atm.}$, $T = 573^\circ\text{K.}$, $N_n^\circ = 0.286$, $N_0^\circ = 0.143$, $r_0 = 2$, and

$$R = 1.315 \text{ cu. ft.-atm./deg. C.};$$

therefore,

$$\begin{aligned} C_1 &= 2.10 & C_2 &= 1.99 \\ C_3 &= 4.44 & C_4 &= 0.0556. \end{aligned}$$

At equilibrium,

$$0.264 = \frac{(x - y)^2 x}{(1 - x)^2} \quad (12.40)$$

$$319.2 = \frac{y^2}{(x - y)^2 (1 - y)}, \quad (12.41)$$

and by trial-and-error solution, it is found that 85 mole per cent of the NOCl will be decomposed and 76.5 per cent of the O_2 will be consumed at equilibrium. Thus a small, unimportant increase in volume occurs owing to incomplete oxidation of the NO .

In order to apply Eqs. (12.35) and (12.36) to the computation of converter volume, simple stepwise numerical integration will be resorted to, since it is doubtful whether this pair of simultaneous differential equations possess an analytical solution. It will be necessary to assume a small extent of reaction in the preheater used to heat the reaction mixture up to 300°C. , before entering the converter. Assuming $x_0 = 0.10$ and $y_0 = 0.02$, the problem is to compute the converter height required to attain $x = 0.80(0.85) = 0.68$.

The equations for numerical integration are

$$\frac{dx}{dh} = 2.10(1 - x)^2 - 7.96(x - y)^2 x. \quad (12.42)$$

$$\frac{dy}{dh} = 17.76(x - y)^2(1 - y) - 5.56 \cdot 10^{-2} y^2. \quad (12.43)$$

When $h = 0$, $x_0 = 0.10$, $y_0 = 0.02$,

$$\left(\frac{dx}{dh}\right)_0 = 2.1(0.81) - 7.96(64)10^{-4}(0.1) = 1.70 - 0.005 = 1.695.$$

$$\left(\frac{dy}{dh}\right)_0 = 17.7(64)10^{-4}(0.98) - 0 = 0.111.$$

At a distance 0.02 ft. above the base of the converter

$$x_{0.02} = 0.10 + \left(\frac{dx}{dh}\right) \Delta h = 0.10 + 1.695(0.02) = 0.134.$$

$$y_{0.02} = 0.02 + \left(\frac{dy}{dh}\right) \Delta h = 0.02 + 0.111(0.02) = 0.0222.$$

The rates of change of x and y at this point are, then,

$$\left(\frac{dx}{dh}\right)_{0.02} = 2.1(0.866)^2 - 7.96(0.112)^2(0.134) = 1.564.$$

$$\left(\frac{dy}{dh}\right)_{0.02} = 17.76(0.112)^2(0.978) = 0.218.$$

If an average of the initial and final rates is used for this interval, the values of $x_{0.02}$ and $y_{0.02}$ become

$$x_{0.02} = 0.10 + \left(\frac{dx}{dh}\right)_{av.} \Delta h = 0.10 + 1.63(0.02) = 0.133.$$

$$y_{0.02} = 0.02 + \left(\frac{dy}{dh}\right)_{av.} \Delta h = 0.02 + 0.165(0.02) = 0.023.$$

A comparison of the two pairs of values for x and y shows that the values computed from the initial rates do not differ greatly from those based on the average of the rates at the beginning and the end of the interval, and hence initial rates with small intervals will be employed for carrying out the integration. The results of these calculations are summarized in Table 1. It should be noted that values for dx/dh and dy/dh represent the rates at the beginning of the indicated interval and were used to compute values for x and y at the end of the indicated interval. In all cases the recorded values of x and y represent the values of these variables at the total height indicated by the figure in the same row with any pair of values of x and y .

Examination of the figures in Table 1 shows that a converter having a volume of about 1.25 cu. ft. should effect the required oxidation. The accuracy of this estimate depends to a large extent on the soundness of the assumed mechanism and the applicability of the low-pressure reaction-rate constants to a pressure system. The uncertainties introduced by applying reaction-rate constants, obtained on static systems, to flow systems are also present but unavoidable. Furthermore, the assump-

tion of no catalytic effects due to the walls of the converter may or may not be reliable. On the whole, a computation of this sort is probably accurate to within the customary engineering factor of safety, and the extension of the method to a wide variety of conditions of temperatures, pressures, and concentrations should lead to results of correct comparative significance.

TABLE 1.—THE RATE OF OXIDATION OF NOCl AT 300°C. AND 5 ATMOSPHERE PRESSURE

| Interval | Δh , (ft.) | Total height, ft. | $\frac{dx}{dh}$ | $\frac{dy}{dh}$ | Fraction NOCl decomposed, x | Fraction O ₂ consumed, y |
|----------|--------------------|-------------------|-----------------|-----------------|-------------------------------|---------------------------------------|
| | | 0 | | | 0.100 | 0.020 |
| 1 | 0.02 | 0.02 | 1.630 | 0.165 | 0.133 | 0.023 |
| 2 | 0.02 | 0.04 | 1.562 | 0.210 | 0.164 | 0.027 |
| 3 | 0.02 | 0.06 | 1.445 | 0.324 | 0.193 | 0.033 |
| 4 | 0.02 | 0.08 | 1.331 | 0.440 | 0.220 | 0.042 |
| 5 | 0.02 | 0.10 | 1.223 | 0.539 | 0.245 | 0.053 |
| 6 | 0.04 | 0.14 | 1.122 | 0.620 | 0.290 | 0.078 |
| 7 | 0.04 | 0.18 | 0.956 | 0.736 | 0.328 | 0.107 |
| 8 | 0.04 | 0.22 | 0.823 | 0.773 | 0.361 | 0.138 |
| 9 | 0.04 | 0.26 | 0.713 | 0.759 | 0.390 | 0.168 |
| 10 | 0.04 | 0.30 | 0.630 | 0.725 | 0.415 | 0.197 |
| 11 | 0.10 | 0.40 | 0.560 | 0.674 | 0.471 | 0.264 |
| 12 | 0.10 | 0.50 | 0.426 | 0.555 | 0.514 | 0.320 |
| 13 | 0.10 | 0.60 | 0.342 | 0.450 | 0.548 | 0.365 |
| 14 | 0.20 | 0.80 | 0.283 | 0.372 | 0.604 | 0.439 |
| 15 | 0.20 | 1.00 | 0.198 | 0.261 | 0.644 | 0.492 |
| 16 | 0.25 | 1.25 | 0.148 | 0.196 | 0.681 | 0.541 |

The time of detention corresponding to the estimated converter volume and gas flows is

$$\Delta t = \frac{1.25 \cdot 3,600 \cdot 5}{3.5 \cdot 1.315 \cdot 573} = 8.5 \text{ sec.}$$

The preceding illustration demonstrates a quantitative approach to one class of industrially important reactions, *i.e.*, oxidation processes. The fact that the reaction considered is one of the simplest oxidation reactions known does not detract from its value for illustrative purposes. Of much greater importance is the oxidation of hydrocarbons to various oxygenated products

of commercial value. In this case, unfortunately, the reaction systems are so complex, from both the chemical and the physical standpoints, that practically no data on specific reaction-rate constants of the individual reactions involved are available. Since most of these processes require careful control of temperatures and concentrations in order to obtain maximum efficiencies, it is apparent that such data, coupled with reliable data on heat interchange, would be of great value in designing suitable converters for carrying out oxidation reactions.

A second class of important reactions to be considered is the decomposition of hydrocarbons to produce a variety of lighter molecules of value in industrial organic syntheses. Here, too, only the simplest systems can be treated owing to the paucity of fundamental kinetic data. Owing to the large temperature gradients involved, it is necessary to consider rates of heat transfer, as well as rates of chemical reactions in the converter.

3. Design of "Cracker" for Thermal Decomposition of *n*-Butane. *Illustration 2.*—Ethylene and propylene may be produced by thermal decomposition of *n*-butane. Assuming that butane is to be cracked by passage through a tube heated externally by means of a large excess of hot gases at 560°C., estimate (a) the size of the tube required to effect 25 per cent decomposition of the butane and (b) the composition of the exit gases, under the following operating conditions:

1. Temperature of butane entering tube = 510°C.
2. Internal diameter of steel tube = 3.548 in., external = 4.00 in.
3. Operating pressure = 1 atm.
4. Mass velocity through tube = 101 lb./(hr.)(sq. ft.).

Solution.—*a.* The results of the investigations of Echols and Pease⁵ on the kinetics of the decomposition of *n*-butane will be used as a basis for computation. According to these authors, the rate of decomposition of *n*-butane in a potassium chloride coated bulb is expressed by the semiempirical equation

$$-\frac{dP_B}{dt} = k_1 P_B^{1.5} + \frac{k_2 P_B^2}{P_{0B} - P_B}, \quad (12.44)$$

where P_{0B} represents the initial pressure of butane and P_B the instantaneous pressure of butane. The constants k_1 and k_2 have

the following values when the pressures are expressed in millimeters of mercury and the time in minutes:

| Temperature, °C. | $k_1 \cdot 10^4$ | $k_2 \cdot 10^4$ | - |
|------------------|------------------|------------------|---|
| 480 | 0.642 | 0.182 | |
| 490 | 1.043 | 0.338 | |
| 500 | 1.80 | 0.625 | |
| 510 | 2.85 | 1.126 | |
| 520 | 4.50 | 1.95 | |
| 535 | 8.30 | 4.77 | |

Under the assumed conditions of this problem, a substantial temperature gradient will exist between the reacting gas and the tube wall; therefore it is necessary to set up two differential equations, expressing the gas temperature T and the butane pressure P_B as functions of tube height h . This may be done by means of the following material and enthalpy balances:

- (1) Pound moles butane leaving tube per minute = pound moles entering per minute - pound moles decomposed per minute.
- (2) Enthalpy gained by materials leaving tube per minute = enthalpy gain due to temperature increase of butane + enthalpy gain due to chemical reactions.

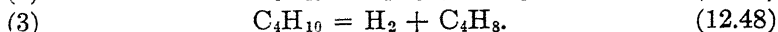
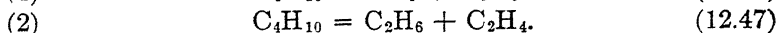
Since in a constant-pressure process the enthalpy increase equals the heat absorbed, the left-hand member of (2) must be equal to the total heat transferred through the walls of the tube to the reacting gas.

The treatment of conditions (1) and (2), in order to obtain the necessary differential equations, follows the procedure discussed in illustration 1. Let n_0 represent the pound moles butane entering the base of each tube per minute and x the fraction of the inlet butane decomposed at any height h above the base of the tube. The partial pressure of the undecomposed butane at the height h is then given by the equation

$$P_B = \left(\frac{1-x}{1+x} \right) P \quad (12.45)$$

where P equals the total pressure on the tube in millimeters of mercury. This equation is based on the assumption that the

following three reactions are the only reactions occurring in the tube:



Differentiation of Eq. (12.45) yields

$$-\frac{dP_B}{dt} = \frac{2P}{(1+x)^2} \frac{dx}{dt}. \quad (12.49)$$

Substitution of Eqs. (12.45) and (12.49) in (12.44) gives

$$\frac{dx}{dt} = \frac{k_1}{2} P^{1/2} (1+x)^{1/2} (1-x)^{1.5} + \frac{k_2(1+x)(1-x)^2}{4x}. \quad (12.50)$$

In accordance with the material balance condition,

$$n_0(1-x) = n_0 - \int_V \left(-\frac{\partial B}{\partial t} \right) dt, \quad (12.51)$$

where $-\partial B/\partial t$ represents the total moles of butane decomposing per minute at the height h , and dt equals the time spent by the gas in the element of volume dV where the gas temperature is T . If S is the cross-sectional area of the tube in square feet, then

$$dt = \frac{PS dh}{n_0(1+x)RT}.$$

Substitution of this expression in Eq. (12.51) and differentiation yield

$$-n_0 \frac{dx}{dh} = \frac{\partial B}{\partial t} \left[\frac{PS}{n_0(1+x)RT} \right]. \quad (12.52)$$

Since $(\partial B/\partial t) = -n_0(dx/dt)$ and dx/dt is given by Eq. (12.50), it follows that

$$\frac{dx}{dh} = \left(\frac{C_1 k_1}{T} \right) \frac{(1-x)^{1.5}}{(1+x)^{0.5}} + \left(\frac{C_2 k_2}{T} \right) \frac{(1-x)^2}{x}, \quad (12.53)$$

where

$$C_1 = \frac{SP^{3/2}}{2n_0R} \quad C_2 = \frac{SP}{4n_0R}.$$

Equation (12.53) is the first of the required equations. The second may be obtained from the enthalpy increase as follows:

The total heat transferred per minute to the gas over the entire tube is obviously given by the relation

$$\int_A \frac{\partial Q}{\partial A} dA = \int_A U(T_e - T)dA, \quad (12.54)$$

where $\partial Q/\partial A$ represents the centigrade heat units transferred per minute per square foot through the element of tube surface dA located at the height h , where the gas temperature is T , and the temperature of the hot gases outside the tube is T_e . U represents the over-all coefficient of heat transfer from the gases at 560°C . to the flowing hydrocarbon gases in the tube. It is, itself, a function of the gas temperature, composition, and flow, and hence a function of the tube height. In order to simplify these computations somewhat, it will be assumed that the major resistance to the flow of heat is offered by the gas film lining the inner wall of the tube. Since the rate of heat consumption is low, and the hot gases are in large excess, it is reasonable to assume that the tube wall is also at 560°C . The problem of computing the rate of heat transfer to the butane then depends on the evaluation of the heat transfer through the gas film of conductivity h_f , neglecting radiation transfer. The total heat transferred through the tube per minute is, therefore,

$$Q = \pi D \int_A h_f(T_e - T)dh. \quad (12.55)$$

The estimation of the gas-film coefficient h_f for the gases in question is uncertain. The Reynolds number (see Chap. XVII) for the specified flows is estimated to be about 600; therefore the flow through the "cracker" is essentially viscous. The film coefficient may be roughly estimated for viscous flow in circular pipes by means of the following empirical relation, given by Walker, Lewis, McAdams, and Gilliland:⁶

$$h = \frac{1.65}{D} \left(\frac{wC_p}{L} \right)^{1/4} k^{3/4}, \quad (12.56)$$

where D = pipe diameter in feet.

w = pounds of gas per hour through pipe.

C_p = specific heat of gas in C.h.u. per pound per degree centigrade.

k = thermal conductivity of gas.

L = length of pipe in feet.

h_f = film conductivity in C.h.u. per hour per degree centigrade per square foot.

Substitution of $D = 0.296$, $w = 6.96$, $C_p = 0.79$, and $k = 0.045$ gives the following equation for h_f , as a function of L :

$$h_f = \frac{0.021}{L^{1/2}}, \quad (12.57)$$

where h_f now represents the centigrade heat units transferred per minute per degree centigrade per square foot. The value of k has been based on the estimated viscosity of butane and its specific heat at these temperatures.

The following values have been computed for h_f , at the indicated heights in the tube:

| | | | | | | | |
|---------------|-------|--------|--------|-------|--------|--------|-------|
| h , ft..... | 1 | 3 | 5 | 7 | 9 | 50 | 325 |
| h_f | 0.021 | 0.0146 | 0.0123 | 0.011 | 0.0101 | 0.0057 | 0.003 |

The foregoing data, although rough, are adequate for estimating Q , the heat transferred to the reacting gases per minute, which is equal to the enthalpy gained by the reactants, as expressed by the equation

$$Q = n_0 \int_{T_0}^T C_p dT + \sum \Delta H_R. \quad (12.58)$$

In this equation, the integral term represents the increase in sensible heat of the butane entering the tube at T_0 and leaving at T . This item may be evaluated by estimating the molar-heat capacity of n -butane, in the temperature range of interest, to be

$$C_p = 6.84 + 0.050T. \quad (12.59)$$

In order to evaluate the enthalpy increment ($\sum \Delta H_R$) accompanying the decomposition reactions, it is necessary to make some assumptions regarding the relative extents of occurrence of reactions (12.46) to (12.48). According to Echols and Pease, the ratios of reactions (1):(2):(3) on page 255 were found to be as 10:4:1 at 520°C., at 25 per cent decomposition. In the absence of any definite mathematical relationship by means of which these ratios could be computed, it will be necessary to assume that these same ratios apply under the conditions of this problem. Thus, if x represents the over-all fraction of butane decomposed,

then the fraction decomposed by reaction (12.46) is $\frac{2}{3}x$; by (12.47), $\frac{4}{15}x$; and by (12.48), $x/15$.

The standard ΔH 's of formation of the compounds involved at 298.1°K. are as follows:

| Compound | $\Delta H_{298.1}$ cal. |
|-----------------------------|-------------------------|
| CH_4 | -17,870 |
| C_2H_4 | +12,590 |
| C_2H_6 | -20,195 |
| C_3H_6 | +4,785 |
| $n\text{-C}_4\text{H}_{10}$ | +400 |
| $n\text{-C}_4\text{H}_{10}$ | -29,755 |

The corresponding heats of reactions (12.46) to (12.48) are, therefore,

$$\begin{aligned}
 (12.46): \Delta H_{298.1} &= 16,670 \text{ cal.} & \Delta C_p &\simeq 0 \\
 (12.47): \Delta H_{298.1} &= 22,150 \text{ cal.} & \Delta C_p &\simeq 0 \\
 (12.48): \Delta H_{298.1} &= 30,155 \text{ cal.} & \Delta C_p &\simeq +5 \\
 \Delta H &= 28,670 + 5T. & & (12.60)
 \end{aligned}$$

Substitution of these data in (12.58) yields the equation

$$Q = n_0 \int_{T_0}^T (6.84 + 0.05T) dT + \frac{2}{3}n_0x(16,670) + \frac{4}{15}n_0x(22,150) + \frac{1}{15}n_0x(28,670 + 5T)$$

or

$$Q = n_0 \int_{T_0}^T (6.84 + 0.05T) dT + \left(18,910 + \frac{T}{3}\right) n_0x. \quad (12.61)$$

Equating (12.55) and (12.61) yields

$$\begin{aligned}
 \pi D \int_A h_f(T_e - T) dh &= n_0 \int_{T_0}^T (6.84 + 0.05T) dT \\
 &+ n_0 \left(18,910 + \frac{T}{3}\right) x \quad (12.62)
 \end{aligned}$$

which, when differentiated, gives

$$\begin{aligned}
 \pi D h_f(T_e - T) dh &= n_0(6.84 + 0.05T) dT \\
 &+ n_0 \left(18,910 + \frac{T}{3}\right) dx + \frac{n_0}{3} x dT. \quad (12.63)
 \end{aligned}$$

Simplification of Eq. (12.63) yields the following desired differential equation for computing the change of gas tempera-

ture with tube height:

$$\frac{dT}{dh} = \frac{\pi D h_f}{n_0} \left(\frac{T_e - T}{6.84 + 0.05T} \right) - \frac{56,730 + T}{3(6.84 + 0.05T)} \left(\frac{dx}{dh} \right). \quad (12.64)$$

Equations (12.53) and (12.64) may now be employed to obtain an approximate solution of the given illustration by the method of simple numerical integration used in the previous illustration. The various constants appearing in these two equations have the following values:

$$\begin{array}{ll} S = 0.0687 \text{ sq. ft.} & R = 1,000 \text{ cu. ft.-mm./deg. C.} \\ D = 0.296 \text{ ft.} & T_e = 560 + 273 = 833^\circ\text{K.} \\ P = 760 \text{ mm.} & C_1 = 357. \\ n_0 = 2 \cdot 10^{-3} \text{ pound mole/min.} & C_2 = 6.53. \end{array}$$

Substituting these values in Eqs. (12.53) and (12.64) yields

$$\begin{aligned} \frac{dx}{dh} &= \left(\frac{357k_1}{T} \right) \frac{(1-x)^{1.5}}{(1+x)^{0.5}} + \left(\frac{6.53k_2}{T} \right) \frac{(1-x)^2}{x} \quad (12.65) \\ \frac{dT}{dh} &= 465h_f \left(\frac{833 - T}{6.84 + 0.05T} \right) - \frac{56,730 + T}{3(6.84 + 0.05T)} \left(\frac{dx}{dh} \right). \end{aligned} \quad (12.66)$$

The appropriate values of k_1 , k_2 , and h_f to be substituted in these equations may be obtained by interpolation from the previously recorded values of these constants.

At the entrance to the tube, $h = 0$, $h_f = 0.021$, $T = 783^\circ\text{K.}$, $k_1 = 2.85 \cdot 10^{-4}$, and $k_2 = 1.126 \cdot 10^{-4}$; therefore

$$\begin{aligned} \frac{dx}{dh} &= 1.30 \cdot 10^{-4} \frac{(1-x)^{1.5}}{(1+x)^{0.5}} + 9.40 \cdot 10^{-7} \frac{(1-x)^2}{x}, \\ \frac{dT}{dh} &= 9.80 \left(\frac{833 - T}{6.84 + 0.05T} \right) - \frac{56,730 + T}{3(6.84 + 0.05T)} \left(\frac{dx}{dh} \right). \end{aligned}$$

If the butane is assumed to be cracked to the extent of 1 per cent at the entrance to the tube, then

$$\left(\frac{dx}{dh} \right)_0 = 2.24 \cdot 10^{-4} \quad \left(\frac{dT}{dh} \right)_0 = 10.6;$$

and the values of x and T at a distance 0.5 ft. above the base of the tube would be approximately

$$\begin{aligned} x_{0.5} &= 0.01 + 2.24 \cdot 10^{-4}(0.5) = 0.0101. \\ T_{0.5} &= 783 + 10.6(0.5) = 788.3^\circ\text{K.} \end{aligned}$$

The corresponding slopes at this point, as calculated from the equations

$$\frac{dx}{dh} = 1.58 \cdot 10^{-4} \frac{(1-x)^{1.5}}{(1+x)^{0.5}} + 1.24 \cdot 10^{-6} \frac{(1-x)^2}{x},$$

$$\frac{dT}{dh} = 9.80 \left(\frac{833 - 788}{46.2} \right) - \frac{57,518}{139} \left(\frac{dx}{dh} \right),$$

are

$$\left(\frac{dx}{dh} \right)_{0.5} = 2.82 \cdot 10^{-4} \quad \left(\frac{dT}{dh} \right)_{0.5} = 9.42.$$

The values of x and T at a distance 1 ft. above the base of the tube are, consequently,

$$x_1 = 0.0101 + 2.82 \cdot 10^{-4}(0.5) = 0.0102.$$

$$T_1 = 788.3 + 9.42(0.5) = 793.0^\circ\text{K}.$$

Proceeding in the above manner, the values for x and T , recorded in Table 2, have been computed as a function of h .

TABLE 2.—THE THERMAL DECOMPOSITION OF *n*-BUTANE AT 510 TO 554°C.

| Interval | Δh , ft. | Total height, ft. | $\left(\frac{dx}{dh} \right) 10^4$ | $\frac{dT}{dh}$ | Fraction butane decomposed, x | Temperature of butane, °C. |
|----------|------------------|-------------------|-------------------------------------|-----------------|---------------------------------|----------------------------|
| | | 0 | | | 0.01 | 510.0 |
| 1 | 0.5 | 0.5 | 2.24 | 10.60 | 0.0101 | 515.3 |
| 2 | 0.5 | 1.0 | 2.82 | 9.42 | 0.0102 | 520.0 |
| 3 | 0.5 | 1.5 | 3.64 | 6.55 | 0.0104 | 523.3 |
| 4 | 0.5 | 2.0 | 4.30 | 5.97 | 0.0106 | 526.3 |
| 5 | 1.0 | 3.0 | 5.13 | 4.72 | 0.0111 | 531.0 |
| 6 | 1.0 | 4.0 | 6.28 | 3.97 | 0.0117 | 535.0 |
| 7 | 2.0 | 6.0 | 7.64 | 2.85 | 0.0132 | 540.7 |
| 8 | 2.0 | 8.0 | 8.79 | 1.79 | 0.0150 | 544.3 |
| 9 | 2.0 | 10.0 | 10.2 | 1.17 | 0.0170 | 546.6 |
| 10 | 5.0 | 15.0 | 10.2 | 0.73 | 0.0221 | 550.3 |
| 11 | 5.0 | 20.0 | 10.6 | 0.36 | 0.0274 | 552.1 |
| 12 | 20.0 | 40.0 | 10.6 | 0.10 | 0.0486 | 554.1 |
| 13 | 20.0 | 60.0 | 9.10 | 0 | 0.0668 | 554.1 |
| 14 | 20.0 | 80.0 | 8.29 | 0 | 0.0834 | 554.1 |
| 15 | 20.0 | 100.0 | 7.72 | 0 | 0.0988 | 554.1 |
| 16 | 50.0 | 150.0 | 7.28 | 0 | 0.1352 | 554.1 |
| 17 | 50.0 | 200.0 | 6.53 | 0 | 0.1679 | 554.1 |
| 18 | 50.0 | 250.0 | 5.95 | 0 | 0.1977 | 554.1 |
| 19 | 50.0 | 300.0 | 5.49 | 0 | 0.2252 | 554.1 |
| 20 | 50.0 | 350.0 | 5.10 | 0 | 0.251 | 554.1 |

Reference to Table 2 shows that a tube 350 ft. long would be required to decompose 25 per cent of the butane, at a mass velocity of 101 lb./(hr.)(sq. ft.). It will be noticed that, with the converter wall maintained at 560°C., the entering gas attains a temperature of 554°C. within 40 ft. and remains substantially constant at this temperature from there on. The temperature gradient of 6 deg. between the tube wall and the gas is just sufficient to permit enough heat to flow into the gas to supply the enthalpy increment required by the endothermic decomposition reactions.

b. The gases leaving the converter would have the following approximate composition:

| Compound | Mole Fraction |
|-------------|---------------|
| C_4H_{10} | 0.5980 |
| C_4H_8 | 0.0133 |
| C_3H_6 | 0.1338 |
| C_2H_6 | 0.0535 |
| C_2H_4 | 0.0535 |
| CH_4 | 0.1338 |
| H_2 | 0.0133 |

The foregoing computed composition, as previously mentioned, has been based on the assumption that the ratios of reactions (12.46) to (12.48) at these temperatures were the same as those given by Echols and Pease for 525°C. Since the average temperature of the converter is not very different from this temperature, and since these ratios do not change too rapidly with temperature, the foregoing composition should be a good approximation to the actual composition for the specified operating conditions.

In view of the large size of converter required to produce only 25 per cent decomposition, it would appear that the production of ethylene and propylene by decomposition of *n*-butane at temperatures around 550°C. is not a promising procedure. Although the rate of decomposition would increase rapidly at still higher temperatures, the experimental evidence indicates that butene formation is favored over the formation of ethylene and propylene at higher temperatures. The formation of carbon, butadiene, and tars would also be favored by elevated temperatures.

The method of simple numerical integration, employed in this chapter to solve systems of simultaneous differential equations, will be used frequently in solving practical problems in this monograph. In view of the many assumptions made in setting up these equations, the use of the more accurate and elaborate integration procedures described in the standard textbooks of differential equations would hardly seem to be warranted. In general, the accuracy of simple numerical integration is adequate for most engineering computations and is considerably more accurate than the use of various types of averages employed in engineering work.

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CHAPTER XIII

GAS ABSORPTION

1. General Considerations.—The design of units used for the absorption of gases in liquid mediums or the stripping of gases from liquid solutions is based on the concept that the major resistance—and, therefore, the factor controlling the rate of transfer of material between the gas and liquid phases—is the presence of a more or less stationary film of material on both sides of the gas-liquid interface. Since these films are assumed to be practically stationary, transfer of matter through these regions can take place only by diffusion; hence the quantitative treatment of absorption problems resolves itself into the application of the laws of diffusion to the transfer of matter through these two films.

The results in the case of a single dilute gas diffusing through a stagnant layer of a second gas are particularly simple. In brief, the rate of diffusion of the absorbable component through each film, expressed as pound moles per unit time per unit area of interface, is given by an expression of the form

$$\frac{dZ}{dA} = \frac{\Delta P}{R}, \quad (13.1)$$

where ΔP is the driving force or concentration gradient across each film responsible for diffusion, and R represents the resistance of each film to diffusion; dA is the area of interface through which dZ pound moles are diffusing per unit time. The reciprocal of the resistance may be replaced by the conductivity k ; thus,

$$\frac{dZ}{dA} = k\Delta P. \quad (13.2)$$

It is sometimes convenient to employ the usual liquid-phase concentration units to evaluate concentration gradients across the liquid film but, when Henry's law may be assumed, it is more convenient to express the diffusion potentials as partial pressures

in atmospheres. When steady-state conditions have been established, the moles diffusing through the gas film per unit time equal the moles diffusing through the liquid film per unit time and, therefore,

$$\frac{dZ}{dA} = k_{(g)}\Delta P_{(g)} = k_{(l)}h\Delta P_{(l)}, \quad (13.3)$$

where h = Henry's law constant (concentration per unit pressure).

$k_{(g)}$ = gas-film absorption coefficient or conductivity.

$k_{(l)}$ = liquor-film coefficient or conductivity.

$\Delta P_{(g)} = P_{(g)} - P_{(i)}$ = difference between the partial pressure of absorbable constituent in gas phase and its pressure at the interface.

$\Delta P_{(l)} = P_{(i)} - P_{(l)}$ = difference between the partial pressure of the absorbable constituent at interface and in the solution.

The rate of mass transfer may also be expressed in terms of the total gradient across the two films and an over-all absorption coefficient. Thus

$$\frac{dZ}{dA} = K_{(g)}\Delta P_T = K_{(g)}(\Delta P_{(g)} + \Delta P_{(l)}). \quad (13.4)$$

Substituting for the individual liquor- and gas-film gradients in terms of Eq. (13.3) gives the following relation between the over-all absorption coefficient and the individual film coefficients:

$$\frac{1}{K_{(g)}} = \frac{1}{k_{(g)}} + \frac{1}{hk_{(l)}}. \quad (13.5)$$

In general, the resistance of both films must be considered, but in certain cases the resistance of one or the other film may be neglected. For example, if the absorbable constituent is very soluble in the absorbent (ammonia in water), h is large and the second term on the right-hand side of (13.5) is negligible compared to the first and $K_{(g)} \simeq k_{(g)}$. In this case, the gas-film resistance predominates and the absorption process is said to be gas film controlled. On the other hand, when the solubility of the absorbable constituent in the absorbent is low (CO_2 in H_2O), the first term is apt to be negligible compared to the second and $K_{(g)} \simeq hk_{(l)}$. This is considered to be a case of liquor film

controlled absorption. The absorption of SO_2 in water is an example of absorption in which both liquor- and gas-film resistance are controlling.

It has been found by experiment that the gas-film coefficient is approximately proportional to the 0.8th power of the mass velocity (linear velocity \times density) of the gas in the turbulent flow region and practically independent of the liquor velocity. It decreases slowly with increasing temperature. The liquor-film coefficient is approximately proportional to the 0.6 – 1.0 power of the liquor flow and independent of the gas flow. As a general rule, the liquor-film coefficient increases sharply with increasing temperature.

As can be seen from Eq. (13.4), the over-all absorption coefficient, $K_{(o)}$, represents the pound moles of gas absorbed per unit area of interface per unit time per unit of driving force. When using over-all coefficients, the driving force for absorption must be evaluated at each level of the absorption unit by taking the difference between the partial pressure of the absorbable constituent in the gas phase and its equilibrium pressure from the liquor, corresponding to the bulk liquor composition at that point. Since it is impossible to predict the effective interfacial area A of a given style of packing from its actual, geometrical surface, it is customary to lump the area factor with $K_{(o)}$ and express the coefficients on a volume basis. Thus

$$dZ = Kga\Delta P_T dV. \quad (13.6)$$

In this equation dV represents an element of absorber volume, ΔP_T the total or over-all driving force, dZ the pound moles absorbed per hour in the section dV , and, therefore, Kga represents the pound moles absorbed per cubic foot per hour per atmosphere of driving force.

The simultaneous absorption of two gases in dilute concentrations from a third, inert gas may be treated as two mutually independent absorption processes, when the respective Kga 's and driving forces are known. The theoretical treatment of simultaneous absorption and desorption is extremely complicated and difficult to treat in a concise fundamentally correct way. In this case, the apparent coefficients of both the absorbed and desorbed gas, when computed by Eq. (13.5), are considerably smaller than those computed when only desorption or absorption

takes place. This reduction in absorption rate is doubtless due to the increased mechanical resistance to diffusion, caused by collisions between molecules streaming through the film in opposite directions. Equation (13.5) may be employed for the design of large units in any of these cases when a few experimental values of Kga have been determined on a small-scale absorption unit, under roughly the same conditions of flows, temperatures, and concentrations visualized for the large unit.

Thermochemical considerations are important in absorption problems from two standpoints. In the first place, since the net rate of absorption at any point in a tower is proportional to the difference between the partial pressure of the absorbable component in the gas phase and the partial pressure of that gas from the liquor phase at that point, a knowledge of equilibrium partial pressures is important in computing instantaneous rates, as well as the ultimate limits of absorption for a given gas composition. This occurs when $P_{(g)} = P_{(l)}$, for then ΔP equals zero. In the second place, since increasing temperatures act adversely on both the net driving force for absorption (by increasing P_l) and the absorption coefficient Kga —if the gas-film resistance is controlling—it is important that the rate of heat generation at each section of a tower is known in advance in order that adequate cooling facilities may be provided to prevent undue temperature increases.

The method of attacking such problems is exemplified by the two illustrations in this chapter. In the first case equilibrium pressures from the absorbent may be assumed negligible from all but the most highly converted liquors; hence the problem of heat generation is of primary importance. In the second case the rate of absorption is at all times controlled by the difference between the gas-phase pressures and the solution pressures, and the rate of heat generation is also considerable. Furthermore, two essentially distinct approaches to the design of absorption equipment are illustrated by these two problems. The first case deals with the absorption of nitrogen oxides in dilute NaOH, at atmospheric pressure, in packed towers for which data are available in the literature for estimating Kga 's. On the other hand, the second problem deals with the absorption of nitrogen oxides in nitric acid at 5 atm. pressure. Since this operation is usually performed in bubble-cap columns, it is necessary to

introduce the concept of the perfect isothermal plate and treat absorption as a stepwise process, in which the gas and liquor leaving each plate are in equilibrium at the instant of separation.

Since nitrogen oxides are very soluble in basic solutions, it might be anticipated in advance of actual experimental data that the rate of absorption of these gases is primarily gas film controlled. This conclusion is confirmed by the results of Chambers and Sherwood¹ on the absorption of NO_2 in dilute NaOH solutions. Furthermore, as long as the absorbing solution remains basic, it is safe to assume the complete absence of any equilibrium oxide pressure exerted by the liquid phase at the gas-liquid interface; therefore the instantaneous rate of absorption at any point in the apparatus should be proportional to the oxide pressure in the gas phase at that point. The analysis of the performance of such a system from an equilibrium standpoint is therefore without significance. In view of the large effect of temperature on the performance of an absorption unit, an accurate analysis of the enthalpy changes taking place at each level of the absorption unit is highly desirable.

The effect of temperature on the performance of an alkaline absorption unit is twofold. In the first place gas-absorption coefficients usually decrease moderately with increasing temperature; in the second place the rate of oxidation of the NO decreases with increasing temperature, and consequently the NO_2 absorption drives decrease with increasing temperature. For these reasons it is desirable to maintain as low temperatures as are consistent with economical heat interchange throughout the absorption system.

The necessary equations for computing the chemical and thermal effects in an absorption unit may be derived from the fact that, at any point in a packed section, the following seven processes are taking place at definite rates:

1. The oxidation of NO to NO_2 in the gas phase.
2. The transfer of NO_2 from the gas to the solution phase.
3. The transfer of NO from the gas to the solution phase.
4. The generation of heat in the gas phase by reaction (1).
5. The generation of heat accompanying the absorption of NO_2 and NO in NaOH .
6. The transfer of sensible heat from the liquid to the gas phase or vice versa.

7. The transfer of water vapor from the liquid to the gas phase or vice versa.

It can be shown that, when the initial quantities, compositions, and temperatures of the gas and liquor entering the section are specified, the system is completely determined at any point a distance h above the base of the unit if the following six variables are known:

N = mole fraction of nitrogen oxides in the gas.

M = mole fraction of O_2 in the gas.

x = state of oxidation of the nitrogen oxides
 $= NO_2/(NO + NO_2)$.

W = mole fraction water vapor in the gas.

tg = temperature of gas.

t = temperature of absorbent liquor.

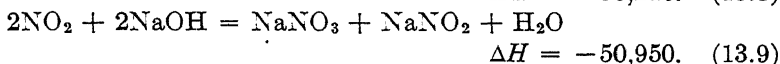
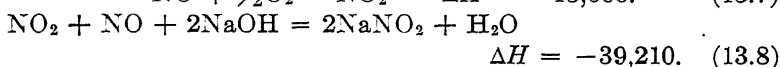
The problem is, therefore, to evolve a set of six simultaneous differential equations by means of which the above unknowns may be expressed as functions of h under conditions of steady flow.

By assuming that heat interchange is effected by means of cooling coils installed between packed sections and that operation within a packed section is substantially adiabatic, the following material and heat balances may be set up:

- (1) Pound moles O_2 leaving section per hour = pound moles O_2 entering per hour - $\frac{1}{2}$ pound mole NO oxidized per hour in section.
- (2) Pound moles oxides leaving section = pound moles oxides entering - pound moles oxides absorbed in section.
- (3) Pound moles NO_2 leaving section = pound moles NO_2 entering - pound moles NO_2 absorbed + pound moles NO oxidized in section.
- (4) Total enthalpy of materials leaving section = total enthalpy of materials entering section.
- (5) Pound moles water vapor in gas leaving section = pound moles in gas entering + pound moles H_2O vaporized from absorbent in section.
- (6) The instantaneous rate of transfer of sensible heat between liquor and gas at any point = the over-all coefficient of heat transfer \times the over-all temperature difference between the two phases.

The foregoing six conditions may be set up algebraically in terms of known coefficients of NO oxidation, oxide absorption,

H₂O evaporation, and heat transfer, and the enthalpies of the substances involved. These conditions may be converted to the desired differential equations, which may be integrated numerically by expressing V in terms of h and differentiating. However, the labor involved in such a procedure is excessive because of the complexity of the equations so derived—particularly the equation deduced from the condition of constant enthalpy. The problem may be simplified somewhat by breaking the absorption unit down into small sections (about 10 ft.) such that the contraction in volume of the gas and the change in humidity of the gas in any one section may be ignored. Furthermore, since gas-film absorption coefficients and the specific reaction rate constants for the oxidation of NO decrease slowly with increasing temperature, no great error should be introduced by estimating an average constant temperature for gas and liquor throughout a given section. Accordingly, the gross adiabatic temperature rise in any section may be computed from known heat capacities and the heat liberated by the following reactions:



The apparent heats of formation of NaOH and NaNO₃ in 5 molal solution have been used to evaluate the foregoing approximate ΔH 's for the absorption reactions. The B-R value for NaNO_{2(aq)} had to be used in the absence of heat of dilution data for this compound.

2. Absorption in Packed Towers. *Illustration 1.*—A tower packed with 3-in. coke is to be used for countercurrent absorption of nitrogen oxides, in dilute sodium hydroxide solution, at 1 atm. pressure. The gas entering the tower at 25°C. has the following composition:

| | Pound moles/(hr.)/ (sq. ft., ground area) |
|------------------|--|
| NO | 0.476 |
| NO ₂ | 0.884 |
| O ₂ | 1.08 |
| N ₂ | 19.6 |
| H ₂ O | 0.66 |

Per square foot of ground area, 3,510 lb. of solution containing 16.65 weight per cent NaOH (5*m*) are fed to the top of the column per hour. For illustrative purposes, consider a packed segment 4 ft. high and compute,

- a. The composition of the gas leaving the segment.
- b. The moles of NO₂ and NO absorbed and O₂ consumed.
- c. The nitrite-nitrate ratio in absorbent leaving the base of the section.
- d. The adiabatic temperature rise of the gas and liquor in the section.

Solution.—The necessary differential equations may be derived from the foregoing material and heat balances (p. 268) as follows:

Let n_0 = pound moles NO + NO₂ in gas entering 1 sq. ft. of tower cross section (ground area) per hour.

m_0 = pound moles O₂ in gas entering 1 sq. ft. of tower per hour.

w_0 = pound moles H₂O in gas entering 1 sq. ft./hr. (assumed constant).

n_i = pound moles N₂ in gas entering 1 sq. ft./hr.

x_0 = state of oxidation of gas entering tower.

N_0 = total mole fraction oxides entering tower.

M_0 = mole fraction oxygen in gas entering tower.

Letters without subscripts represent the corresponding quantities at any height h , above the base of the section.

In order to simplify the computations somewhat, it will be assumed that the association of the NO₂ to N₂O₄, at the concentrations, temperatures, and pressures involved, may be neglected. Conditions (1-3) then become

$$m = m_0 - \frac{1}{2} \int_V \frac{\partial \text{NO}_2}{\partial t} dt. \quad (13.10)$$

$$n = n_0 - \int_V KgaP_{\text{NO}_2} dV - \int_V Kg'aP_{\text{NO}} dV. \quad (13.11)$$

$$nx = n_0x_0 - \int_V KgaP_{\text{NO}_2} dV + \int_V \frac{\partial \text{NO}_2}{\partial t} dt. \quad (13.12)$$

In the foregoing equations Kga and $Kg'a$, respectively, represent the pound moles of NO₂ and NO absorbed per hour per cubic foot per atmosphere driving force of each gas. The integrals are

to be evaluated over the volume of the packed section under consideration. Differentiation of Eqs. (13.10) to (13.12) yields

$$dm = -\frac{1}{2} \frac{\partial \text{NO}_2}{\partial t} dt. \quad (13.13)$$

$$dn = -KgaP_{\text{NO}_2}dV - Kg'aP_{\text{NO}_2}dV. \quad (13.14)$$

$$xdn + ndx = -KgaP_{\text{NO}_2}dV + \frac{\partial \text{NO}_2}{\partial t} dt. \quad (13.15)$$

Assuming that the contraction in gas volume in each individual section is negligible, then

$$dt = \frac{PdV}{\Sigma_0 RT} = \frac{Pf dh}{\Sigma_0 RT}, \quad (13.16)$$

where Σ_0 = total pound moles gas entering base of given section per square foot per hour.

R = 1.315 cu. ft. atm./deg. K.

T = temperature, °K.

P = total pressure = 1 atm.

100 f = per cent free volume in packing.

Substituting Eq. (13.16) in (13.13) to (13.15) yields

$$\frac{dm}{dh} = -\frac{Pf}{2\Sigma_0 RT} \frac{\partial \text{NO}_2}{\partial t}. \quad (13.17)$$

$$\frac{dn}{dh} = -PKga(Nx) - PK'ga[N(1-x)]. \quad (13.18)$$

$$x \frac{dn}{dh} + n \frac{dx}{dh} = -PKga(Nx) + \frac{Pf}{\Sigma_0 RT} \frac{\partial \text{NO}_2}{\partial t}. \quad (13.19)$$

Substituting Eq. (13.18) in (13.19) yields

$$\frac{dx}{dh} = P \frac{Nx}{n} (1-x)(Kg'a - Kga) + \frac{Pf}{\Sigma_0 RTn} \left(\frac{\partial \text{NO}_2}{\partial t} \right). \quad (13.20)$$

From the Bodenstein equation for the rate of oxidation of NO in pressure units,

$$\frac{dP_{\text{NO}_2}}{dt} = kP_{\text{NO}}^2P_{\text{O}_2}, \quad (13.21)$$

where $P_{\text{NO}_2} = NxP = \frac{n}{\Sigma_0} xP. \quad (13.22)$

$$P_{\text{NO}} = N(1-x)P. \quad (13.23)$$

$$P_{\text{O}_2} = MP. \quad (13.24)$$

Since $\partial \text{NO}_2 / \partial t = n(\partial x / \partial t)$, it follows from Eqs. (13.21) to (13.24) that

$$\frac{\partial \text{NO}_2}{\partial t} = kP^2 \sum_0 N^2(1-x)^2 M. \quad (13.25)$$

Substituting Eq. (13.25) and mole fractions in Eqs. (13.17), (13.18), and (13.20) finally yields the required equations for computing the change of M , N , and x with tower height,

$$-\frac{dM}{dh} = \frac{C_1}{2} N^2(1-x)^2 M, \quad (13.26)$$

where $C_1 = \frac{kP^2 f}{\sum_0 RT}$;

$$-\frac{dN}{dh} = C_2 Nx + C_3 N(1-x), \quad (13.27)$$

where $C_2 = \frac{PKga}{\sum_0}$, and $C_3 = \frac{PK'ga}{\sum_0}$;

$$\frac{dx}{dh} = (C_3 - C_2)(1-x) + C_1 N(1-x)^2 M. \quad (13.28)$$

It should be noted that the development of Eqs. (13.26) to (13.28) is predicated on the assumption that the moles of NO_2 present always exceed the moles of NO ($x > 0.50$), since it is impossible to absorb NO without the absorption of an equivalent amount of oxidizing agent (NO_2).

In view of the possibility that this system of simultaneous differential equations may not possess an analytical solution, simple numerical integration will be used in order to obtain the desired data.

Evaluation of Constants.—As explained in illustration 1, Chap. XII, the Bodenstein constants (k_B), for the rate of oxidation of NO , may be converted to pressure units, with time in hours, by multiplying k_B by the factor $3,600/2(0.08206)^2 T^2$. At 25°C ., k_B equals $2.88 \cdot 10^4$; therefore, $k = 8.68 \cdot 10^4$.

The data of Chambers and Sherwood¹ on the absorption of NO_2 in dilute NaOH in a wetted-wall absorption unit may be used to estimate Kga and $Kg'a$ for a coke-packed tower, by the following procedure:

According to simple kinetic theory, the gas-film absorption coefficient for a dilute component diffusing through a stagnant

layer of a second gas is given by the expression

$$kg = \frac{D}{RTB}, \quad (13.29)$$

where B is the film thickness and D is the diffusivity of the diffusing component in the mixture. Chambers and Sherwood compared the rate of absorption of NO_2 , from NO_2 -air mixtures, in NaOH solution with the rate of evaporation of H_2O into air from water in the same apparatus. At 25°C ., they found

$$\frac{B_{\text{H}_2\text{O}}}{B_{\text{NO}_2}} = 0.19$$

in the region of turbulent flow; consequently

$$kg(\text{NO}_2) = kg(\text{H}_2\text{O}) \frac{D_{\text{NO}_2}}{D_{\text{H}_2\text{O}}} (0.19).$$

The ratio $D_{\text{NO}_2}/D_{\text{H}_2\text{O}}$ in air may be estimated from the empirical equation for D , given by Sherwood.^{2,p.18} At 25° and 1 atm. this ratio has the value 0.64 and, therefore,

$$kg(\text{NO}_2) = 0.12kg(\text{H}_2\text{O}).$$

Sherwood^{2,p.178} gives the following equation for computing water coefficients in a tower packed with 3-in. coke:

$$Kga = 0.23G^{0.8}, \quad (13.30)$$

where G represents the pounds of gas entering 1 sq. ft. of tower cross section (ground area) per hour. For the flows, specified in this problem, $G = 651$, and therefore $Kga(\text{H}_2\text{O}) = 41$. The corresponding value for NO_2 should therefore be about 4.91. Coefficients computed from Eq. (13.30) have been based on absorption drives expressed as pound moles of absorbable constituent per pound mole of air. The value 4.91 must be adjusted to convert to absorption drives in atmospheres, giving about 5.1 for the required $Kga(\text{NO}_2)$.

In order to obtain an approximate value for $Kg'a(\text{NO})$, the relation given by Sherwood^{2,p.162} for wetted-wall towers will be assumed to hold for the coke-packed towers; therefore,

$$\frac{Kg'a(\text{NO})}{Kga(\text{NO}_2)} = \left(\frac{D_{\text{NO}}}{D_{\text{NO}_2}} \right)^{0.56}. \quad (13.31)$$

The ratio of diffusivities at 25°C. equals 1.20; hence

$$Kg'a(\text{NO}) = 1.11Kga(\text{NO}_2). \quad (13.32)$$

The required NO absorption coefficient is approximately 5.7 lb. moles/(hr.)(cu. ft.)(atm.) NO driving force.

The constants in Eqs. (13.26) to (13.28) may now be evaluated if a value of 50 per cent is used for the free volume in the coke-packed section.

$$C_1 = \frac{kP^3f}{\Sigma_0 RT} = 4.88.$$

$$C_2 = \frac{PKga}{\Sigma_0} = 0.224.$$

$$C_3 = \frac{PKg'a}{\Sigma_0} = 0.251.$$

Substitution of these values in Eqs. (13.26) to (13.28) yields the required equations for performing the numerical solution of the problem:

$$-\frac{dM}{dh} = 2.44N^2(1-x)^2M. \quad (13.33)$$

$$-\frac{dN}{dh} = N(0.251 - 0.027x). \quad (13.34)$$

$$\frac{dx}{dh} = 0.027x(1-x) + 4.88N(1-x)^2M. \quad (13.35)$$

a. Equations (13.33) to (13.35) may be used to compute the composition of the gas leaving the 4-ft. segment as follows: The technique of simple numerical integration has already been demonstrated in Chap. XII. Starting with $M_0 = 0.0476$, $N_0 = 0.06$, and $x_0 = 0.65$, the rates of change M , N , and x are computed for $h = 0$. Thus,

$$\begin{aligned} \left(-\frac{dM}{dh}\right)_0 &= 5.13 \cdot 10^{-5}, \\ \left(-\frac{dN}{dh}\right)_0 &= 1.4 \cdot 10^{-2}, \\ \left(\frac{dx}{dh}\right)_0 &= 7.86 \cdot 10^{-3}. \end{aligned}$$

The approximate values of M , N , and x at a distance 1 ft. above the base of the section are, therefore,

$$M_1 = 0.0476 - 5.13 \cdot 10^{-5}(1) = 0.04755.$$

$$N_1 = 0.060 - 1.4 \cdot 10^{-2}(1) = 0.0460.$$

$$x_1 = 0.650 + 0.00786(1) = 0.6579.$$

The corresponding rates of change of M , N , and x at this point are

$$\left(-\frac{dM}{dh}\right)_1 = 2.87 \cdot 10^{-5},$$

$$\left(-\frac{dN}{dh}\right)_1 = 1.07 \cdot 10^{-2},$$

$$\left(\frac{dx}{dh}\right)_1 = 7.33 \cdot 10^{-3}.$$

Therefore, at a distance 2 ft. above the base,

$$M_2 = 0.04755 - 0.00003 = 0.04752,$$

$$N_2 = 0.0460 - 0.0107 = 0.0353,$$

$$x_2 = 0.6579 + 0.0073 = 0.6652.$$

Proceeding in this manner, it will be found that the gas leaving the 4-ft. segment of packing has the approximate composition

$$M_4 = 0.0475 = \text{mole fraction of O}_2,$$

$$N_4 = 0.0208 = \text{mole fraction of oxides},$$

$$x_4 = 0.679 = \text{state of oxidation of oxides}.$$

b. The moles of NO_2 and NO absorbed and the moles of O_2 consumed in the 4-ft. segment may be computed by substituting the appropriate values in Eqs. (13.10) to (13.12) and solving. Values so obtained are

$$\text{Pound moles NO}_2 \text{ absorbed per hour} = 0.565,$$

$$\text{Pound moles NO absorbed per hour} = 0.322,$$

$$\text{Pound moles O}_2 \text{ consumed per hour} = 0.002.$$

c. The nitrite-nitrate ratio produced in the absorbing sodium hydroxide solution would be

$$\frac{\text{NaNO}_2}{\text{NaNO}_3} = \frac{1.5(0.322) + 0.5(0.565)}{0.5(0.565 - 0.322)} = 6.29.$$

d. The total heat generated per hour by oxidation and absorption may be computed from Eqs. (13.7) to (13.9).

| | |
|--|-----------------|
| Oxidation: (0.004)(13,560) | = 54.2 C.h.u. |
| Absorption of NO: (0.322)(39,210) | = 12,600 C.h.u. |
| Absorption of NO ₂ : $\frac{1}{2}(0.565 - 0.322)(50,950)$ | = 6,200 C.h.u. |
| Total C.h.u. generated per hour | = 18,850. |

Estimating the heat capacity of the gas phase to be 7.2 C.h.u./(lb. mole)(deg.) and the heat capacity of the solution to be 0.84 C.h.u./(lb.)(deg.), gives the following value for the adiabatic temperature rise above 25°C., in the 4-ft. section:

$$\Delta t = \frac{18,850}{(22.7)(7.2) + (3,510)(0.84)} = \frac{18,850}{3,114} = 6.05^{\circ}\text{C}.$$

Under the conditions chosen for this example, very little heat is generated in the gas phase due to oxidation; consequently, the bulk of the temperature rise will be found in the liquor leaving the bottom of the section. Thus, if there were no transfer of sensible heat or H₂O from the liquid to the gas phase, the temperature of the liquor leaving the section would approach

$$25 + \frac{18,800}{2,950} = 31.4^{\circ}\text{C}.$$

With an over-all coefficient of heat transfer from the liquor to the gas phase of 35 C.h.u./(cu. ft.)(deg. C)(hr.), the gas temperature leaving the section would probably be about 27°C.

The conditions of the foregoing illustration have been deliberately simplified in order not to obscure the application of the fundamental principles involved. In practice, of course, the most highly converted absorbent would be contacted with the most concentrated gases; consequently, the absorption coefficients Kga and $Kg'a$ would be a great deal smaller than those used in these calculations. That would mean that the actual pound moles absorbed in the section would be considerably less and the adiabatic temperature rise correspondingly smaller. Furthermore, the contraction in volume, due to oxide absorption, would be correspondingly smaller, and the assumption of constancy of gas volume and temperature in the section under consideration would be justified. In carrying the calculations forward to the next section above, temperatures and gas volumes must be adjusted in accordance with the net result of processes occurring in the first section. The extrapolation of Chambers and Sherwood's data on the absorption of NO₂ in a small wetted-

wall column to a commercial packed tower is admittedly inaccurate but is satisfactory for illustrative purposes.

3. Absorption in Bubble-cap Towers. *Illustration 2.*—On the basis of the following data and assumptions, compute

a. The number of perfect plates required to produce 1 ton of nitric acid per day (as 60 weight per cent) with an absorption efficiency of 85 per cent.

b. The heat that must be withdrawn per hour from each plate in order to hold the temperature of the system at the assigned value:

1. Operating pressure = 5 atm. absolute.

2. Operating temperature = 45°C.

3. Tower diameter (*I.D.*) = 6.0 in.

4. Distance from top of liquor on any plate to bottom of next higher plate = 24 in.

5. 77.3 lb. of 25 per cent HNO_3 to feed plate per hour.

6. 6.7 lb. water added to top of column per hour.

7. Pound moles gas entering base of tower per hour,

$$\begin{array}{ll}\text{NO} = 0.077, & \text{N}_2 = 14.84, \\ \text{NO}_2 = 1.115, & \text{H}_2\text{O} = 0.22. \\ \text{O}_2 = 0.782,\end{array}$$

For simplicity, assume that all materials entering and leaving the tower are at 45°C. and that the gas is saturated with H_2O corresponding to the vapor pressure of 25 per cent HNO_3 at 45°C.

Solution.—Since the quantity and composition of the gas entering and the liquor leaving the bottom plate of the tower have been specified, the problem resolves itself into the computation of the composition of the gas leaving and the liquor entering the bottom plate. From the Bodenstein data on the rate of oxidation of NO, the change in gas composition between plates may be estimated and the process repeated on each succeeding plate until the required quantity of nitrogen oxides has been absorbed. In effect, therefore, it is necessary to evaluate the following unknown quantities for each plate:

a. The fraction of total inlet oxides absorbed on any given plate (z_i).

b. The state of oxidation ($100x_i$) of the gas leaving the surface of the liquor on the i th plate.

c. The fraction of the total NO_2 associated to form $\text{N}_2\text{O}_4(y_i)$ in the gas leaving the liquor surface.

d. The composition of the acid overflowing from the $(i + 1)$ plate.

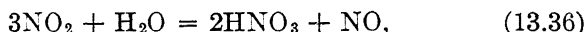
e. The increase in state of oxidation (Δx_i) of the gas in the empty space between plates.

f. The total heat generated (ΔH) per hour in the region between the liquor surface of the i th plate and liquor surface on the $(i + 1)$ plate.

The following set of six equations will be shown to be adequate for the evaluation of the required data if it be assumed that

1. The gas and liquor leaving each plate are in thermodynamic equilibrium with each other.

2. The reactions



are the only reactions occurring in the system.

3. The plates are provided with adequate cooling coils so that the heat generated is removed as fast as it is generated. In other words, isothermal operation is assumed.

On the basis of Eq. (13.36), it follows that for every 3 moles of NO_2 absorbed on the i th plate 1 mole of NO is desorbed and, therefore,

Moles NO_2 leaving i th plate = moles NO_2 entering plate $-\frac{3}{2}$
net moles of oxides absorbed on
plate.

This leads to the first of the required equations,

$$x_i = \frac{(1 - f_{i-1})x_i^e - 1.5z_i}{1 - f_i}, \quad (13.39)$$

where x_i = state of oxidation of gas leaving surface of liquor on the i th plate.

x_i^e = state of oxidation of gas entering vapor riser of the i th plate.

z_i = fraction of total moles oxides entering base of column per hour absorbed on i th plate.

f_{i-1} = fraction of total inlet oxides absorbed up to but not including i th plate.

f_i = fraction of total inlet oxides absorbed up to and including i th plate.

$$z_i = f_i - f_{i-1}.$$

This equation also implies that the oxidation of NO, in accordance with Eq. (13.37), is negligible in the bubble cap itself.

Since the gas and liquor leaving each plate are assumed to be in equilibrium, the equilibrium constant for reaction (13.36) may also be employed. Thus,

$$K_1 = \frac{P_{\text{NO}}(\text{HNO}_3)^2}{P_{\text{NO}_2}^3(\text{H}_2\text{O})} = \frac{P_{\text{NO}}}{P_{\text{NO}_2}^3} \rho. \quad (13.40)$$

If n_0 = pound moles $\text{NO} + \text{NO}_2 + 2\text{N}_2\text{O}_4$ entering the tower per hour, and x_0 and y_0 are the states of oxidation and NO_2 association, respectively, of the inlet oxides, the inlet mole fraction of oxides equals

$$N_0 = \frac{n_0}{\Sigma_0} = \frac{n_0}{n_0 \left(1 - \frac{x_0 y_0}{2}\right) + (\text{O}_2 + \text{N}_2 + \text{H}_2\text{O})_0},$$

and the mole fraction of oxides in the gas leaving the i th plate is

$$N_i = \frac{n_0(1 - f_i)}{\Sigma_i}. \quad (13.41)$$

But

$$\Sigma_i \simeq \Sigma_0 - n_0 f_i,$$

and substituting $n_0 = N_0 \Sigma_0$ in Eq. (13.41) gives

$$N_i = \frac{N_0(1 - f_i)}{1 - N_0 f_i}. \quad (13.42)$$

Consequently, the individual oxide pressures in the gases leaving the i th plate are given by the equations

$$P_{\text{NO}} = \frac{N_0(1 - f_i)(1 - x_i)P}{1 - N_0 f_i}. \quad (13.43)$$

$$P_{\text{NO}_2} = \frac{N_0(1 - f_i)x_i(1 - y_i)P}{1 - N_0 f_i}. \quad (13.44)$$

$$P_{\text{N}_2\text{O}_4} = \frac{N_0(1 - f_i)x_i y_i P}{2(1 - N_0 f_i)}. \quad (13.45)$$

Substituting for P_{NO} and P_{NO_2} in Eq. (13.40) yields the second required relation

$$\frac{K_1 P^2 N_0^2}{\rho} = \left(\frac{1 - N_0 f_i}{1 - f_i} \right)^2 \frac{(1 - x_i)}{[(1 - y_i)x_i]^3} = E. \quad (13.46)$$

The third required relation is given by the equilibrium constant for the association of NO_2 to N_2O_4 , namely,

$$K_2 = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{y_i}{2N_{,x_i}(1 - y_i)^2 P}. \quad (13.47)$$

Substituting $B_i = 1/2N_{,x_i}K_2P$ and solving in the usual way give

$$y_i = \frac{1}{2}(2 + B_i) \pm \frac{1}{2}[(2 + B_i)^2 - 4]^{1/2}. \quad (13.48)$$

At 45°C. , K_2 equals 1.56.

A fourth relationship may be obtained from the gas-liquid material balance at each plate in the tower. That is, for a given quantity and concentration of feed acid, water, and moles of oxides entering the tower per hour, a definite relation must exist between the composition and quantity of acid overflowing from a given plate and the moles of oxides rising from that plate.

Pound moles HNO_3 leaving tower per hour = pound moles HNO_3 overflowing from i th plate + pound moles oxides absorbed up to and including the $(i - 1)$ plate.

Pounds acid leaving tower per hour = pounds acid overflowing from i th plate + increase in weight due to absorption on the $(i - 1)$ lower plates.

Expressed algebraically, these conditions yield the equation

$$f_{i-1} = f_i - z_i = \frac{L_1(w_1 - w_i)}{n_0(63 - 54w_i)}, \quad (13.49)$$

where $100w_1$ = weight per cent HNO_3 in finished acid leaving base of column.

$100w_i$ = weight per cent HNO_3 in acid overflowing from i th plate.

L_1 = pounds of acid leaving column per hour.

Equation (13.49) applies below the feed plate. The following equation is to be used above the feed plate:

$$f_{0+n} - z_{0+n} = \frac{L_{0+1}(w_{0+1} - w_{0+n})}{n_0(63 - 54w_{0+n})}, \quad (13.50)$$

where L_{0+1} = pounds acid overflowing from first plate above feed plate (0 plate).

$100w_{0+1}$ = weight per cent HNO_3 in acid overflowing from first plate above feed plate. ,

$100w_{0+n}$ = weight per cent HNO_3 in acid overflowing from n th plate above feed plate.

f_{0+n} = fraction of total inlet oxides absorbed above feed plate up to and including the n th plate.

z_{0+n} = fraction total inlet oxides absorbed by n th plate above feed plate.

The calculation of the reoxidation of the NO between plates is an important item and may be attempted as follows:

The pound moles NO_2 entering vapor riser of $(i + 1)$ plate per hour = pound moles NO_2 leaving liquor surface on i th plate + pound moles NO oxidized in space between plates.

Expressed algebraically, this becomes

$$n_0(1 - f_i)x_{i+1} = n_0(1 - f_i)x_i + \int_V \left(-\frac{\partial \text{NO}}{\partial t} \right) dt, \quad (13.51)$$

where V represents the free volume between plates. Differentiation of Eq. (13.51) yields

$$n_0(1 - f_i)dx = \left(-\frac{\partial \text{NO}}{\partial t} \right) dt. \quad (13.52)$$

But

$$dt = \frac{PdV}{\Sigma_i RT} \simeq \frac{PA dh}{(\Sigma_0 - n_0 f_i) RT}, \quad (13.53)$$

where A is the cross-sectional area of the column. Substituting $n_0 = N_0 \Sigma_0$ in Eq. (13.53) and substituting for dt in (13.52) yield

$$\frac{dx}{dh} = \left(-\frac{\partial \text{NO}}{\partial t} \frac{PA}{\Sigma_0^2 N_0 (1 - f_i) (1 - N_0 f_i) RT} \right) \quad (13.54)$$

for the rate of change of state of oxidation with height in the region between the i th and $(i + 1)$ plate. The coefficient $-\partial \text{NO} / \partial t$ may be evaluated from Eq. (13.21)

$$-\frac{\partial P_{\text{NO}}}{\partial t} = kP_{\text{NO}}^2 P_{\text{O}_2}, \quad (13.55)$$

where $P_{\text{NO}} = N_i(1 - x)P$

$$P_{\text{O}_2} = \left\{ \frac{2N_0^\circ - N_0[f_i(1.5 - x_i) - (x_0 - x_i)]}{2(1 - N_0 f_i)} \right\} P \quad (13.56)$$

and N_0° represents the mole fraction O_2 entering the tower. The equation for the mole fraction of O_2 in the gas leaving the i th plate may readily be derived by noting that for every mole of NO oxidized, $\frac{1}{2}$ mole of O_2 is consumed, and the moles of NO leaving the i th plate equal total moles NO entering tower, plus $\frac{1}{2}$ total moles oxides absorbed, minus total moles NO oxidized up to the i th plate. Substituting P_{NO} and P_{O_2} in Eq. (13.55) gives

$$N_i \frac{\partial x}{\partial t} = \frac{kP^2}{2} N_i^2 (1 - x)^2 \left\{ \frac{2N_0^\circ - N_0[f_i(1.5 - x) - (x_0 - x)]}{1 - N_0 f_i} \right\}. \quad (13.57)$$

But moles $\text{NO} = N_i \Sigma_i (1 - x)$ and, therefore,

$$-\frac{\partial \text{NO}}{\partial t} = N_i \Sigma_i \frac{\partial x}{\partial t}. \quad (13.58)$$

Consequently the right-hand side of Eq. (13.57), multiplied by Σ_i , gives the required value for $-\partial \text{NO} / \partial t$, to be substituted in (13.54) for computing dx/dh . Substituting in Eq. (13.54) and collecting constants give the desired equation for computing oxidation in the space between any given pair of plates where the total concentration of oxides is constant:

$$\frac{dx}{dh} = \frac{C_5 N_i^2 (1 - x)^2 \{2N_0^\circ - N_0[f_i(1.5 - x) - (x_0 - x)]\}}{(1 - f_i)(1 - N_0 f_i)}, \quad (13.59)$$

where $C_5 = P^2 A k / 2 \Sigma_0 N_0 R T$. This is the fifth required relation. Thus, when f_i and x_i have been evaluated with the help of Eqs. (13.39), (13.46), and (13.49), the dx/dh corresponding to these values may be computed. If dx/dh is not large, the value of x_{i+1}^e may be computed from the relation

$$x_{i+1}^e = x_i + \left(\frac{dx}{dh} \right)_i \Delta h. \quad (13.60)$$

If dx/dh is large, the distance between any two plates should be broken down into small intervals and x_{i+1}^e computed by stepwise integration of Eq. (13.59), using values of x computed by means of Eq. (13.60).

The sixth and final relation is the equation for computing the total heat generated between the surface of the liquor on the i th plate and the surface of the liquor on the $(i + 1)$ plate. This relation is essential for the estimation of the amount of cooling coils that must be installed in each individual plate in order that isothermal operation may be maintained throughout the column and disadvantageous temperature rises prevented. Since, for the purpose of this analysis, it has been assumed that each plate is equipped with adequate cooling facilities so that no appreciable temperature changes occur, it follows that the heat liberated across any given plate is simply the difference between the total enthalpies of formation of the materials leaving the surface of the $(i + 1)$ plate, minus the total enthalpies of formation of the materials entering the plate. In this case the boundaries of the $(i + 1)$ plate are represented by the surfaces of the liquor on the i th and $(i + 1)$ plate.

If the moles of NO , NO_2 , N_2O_4 , HNO_3 , and H_2O entering the $(i + 1)$ plate per hour are multiplied by their respective heats of formation and summed and then deducted from the corresponding sum for the products leaving the $(i + 1)$ plate, the following equation is obtained for ΔH —the heat liberated per hour across the $(i + 1)$ plate:

$$\begin{aligned} \frac{\Delta H}{n_0} = \Delta(f) & \left(\Delta H_{\text{HNO}_3} - \frac{\Delta H_{\text{H}_2\text{O}}}{2} - \Delta H_{\text{NO}} \right) \\ & + (\Delta H_{\text{NO}_2} - \Delta H_{\text{NO}})[\Delta(x) - \Delta(fx)] \\ & + \left(\frac{\Delta H_{\text{N}_2\text{O}_4}}{2} - \Delta H_{\text{NO}_2} \right) [\Delta(xy) - \Delta(xfy)], \quad (13.61) \end{aligned}$$

where $\Delta(f) = f_{i+1} - f_i$.

$\Delta(x) = x_{i+1} - x_i$.

$\Delta(fx) = (fx)_{i+1} - (fx)_i$.

$\Delta(xy) = (xy)_{i+1} - (xy)_i$.

$\Delta(xfy) = (xfy)_{i+1} - (xfy)_i$.

Substituting

$\Delta H_{\text{NO}} = 21,526 \text{ C.h.u./lb. mole,}$

$\Delta H_{\text{NO}_2} = 7,964 \text{ C.h.u./lb. mole,}$

$\Delta H_{\text{N}_2\text{O}_4} = 2,235 \text{ C.h.u./lb. mole,}$

$\Delta H_{\text{H}_2\text{O}} = -68,315 \text{ C.h.u./lb. mole,}$

transforms Eq. (13.61) into convenient form for numerical calculations:

$$\frac{\Delta H}{n_0} = \Delta(f)(\Delta H_{\text{HNO}_3} + 12,630) + 13,560[\Delta(fx) - \Delta(x)] \\ + 6,850[\Delta(xfy) - \Delta(xy)]. \quad (13.62)$$

In using this equation, a value for the heat of formation of HNO_3 corresponding to the average acid concentration on the plate should be used. Values of ΔH_{HNO_3} for various weights per cent nitric acid are plotted on Fig. 17. Strictly speaking, the heats of formation of all compounds should be corrected from the above 25° values to $45^\circ\text{C}.$, as well as from 1 to 5 atm., by means of Eq. (2.18). However, for most engineering purposes these corrections are unimportant.

Equations (13.39), (13.46), (13.48), (13.49), (13.59), and (13.62) provide the requisite tools for solving the given problem. Unfortunately, it is necessary to solve for the unknowns z_i , x_i , y_i , and w_i by trial and error; consequently, the computations are somewhat tedious, as shown by the following sample calculations.

PLATE 1. Initial Conditions:

$$\begin{aligned} L_1 &= 138.5 \text{ lb. acid leaving tower per hour.} \\ 100w_1 &= 60 \text{ per cent } \text{HNO}_3 \text{ in overflow from bottom plate.} \\ N_0 &= 0.07. & y_0 &= 0.377. \\ N_0^\circ &= 0.0459. & \Sigma_0 &= 17.03. \\ x_0 &= 0.935. \end{aligned}$$

The given value for y_0 may be checked by noting that

$$B_0 = \frac{1}{2N_0x_0K_2P} = \frac{1}{2(0.07)(0.935)(1.56)(5)} = 0.98;$$

and from Eq. (13.48), $y_0 = 0.377$.

The material balance operating line for conditions below the feed plate may be computed from Eq. (13.49):

$$f_i - z_i = \frac{L_1(w_1 - w_i)}{n_0(63 - 54w_i)} = \frac{138.5(0.60 - w_i)}{1.192(63 - 54w_i)}.$$

The results are plotted vs. w_i on Fig. 15.

The second operating line corresponding to the liquid-gas equilibrium may be computed from the left-hand side of Eq. (13.46), in the concentration range of interest. Values of

$$E_i = \frac{K_1P^2N_0^2}{\rho} = \frac{(5.05)(25)(49)10^{-4}}{\rho} = \frac{0.619}{\rho}$$

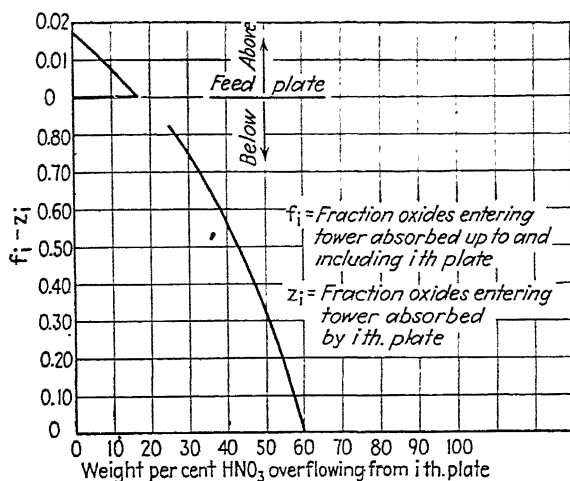
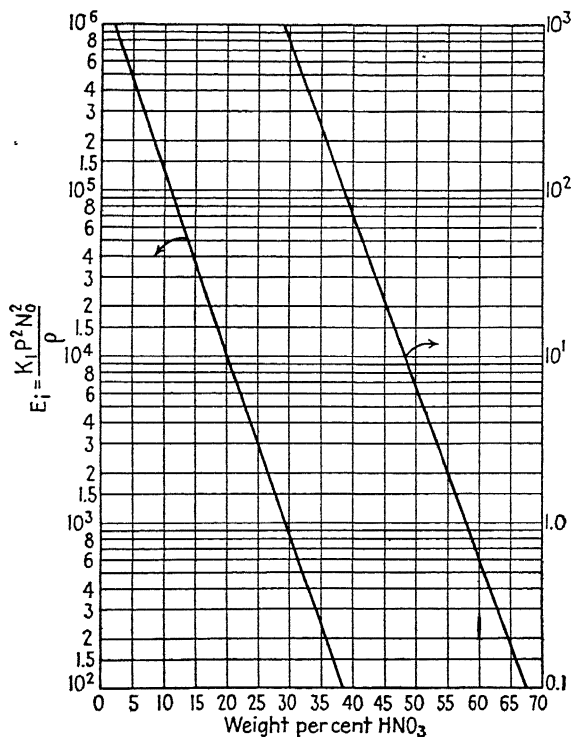


FIG. 15.—Liquid-gas absorption balance at 5 atm. and 45°C.

FIG. 16.— HNO_3 -nitrogen oxides equilibrium at 5 atm. and 45°C.

are plotted against weight per cent HNO_3 on Fig. 16. The necessary values for K_1 and ρ have been taken from illustration 2, Chap. X.

The estimation of the gas composition leaving plate 1 is carried out as follows:

Guess $f_1 = z_1 = 0.06$ = fraction inlet moles oxides absorbed on bottom plate.

$f_1 - z_1 = 0$ and, from Fig. 15, overflow acid = 60 per cent.

From Eq. 13.39,

$x_1 = (0.935 - 0.09)/0.94 = 0.899$ = state oxidation of gas at surface of liquid on bottom plate before gas-phase oxidation can occur.

$N_1 = 0.07(0.94)/0.996 = 0.0662$ = mole fraction oxides in gas rising from bottom plate.

$$B_1 = \frac{6.41 \cdot 10^{-2}}{(0.0662)(0.899)} = 1.080.$$

Therefore $y_1 = 0.368$ = association of NO_2 in gas rising from bottom plate. From Eq. (13.46),

$$E_1 = \left(\frac{0.996}{0.94} \right)^2 \left(\frac{0.101}{0.183} \right) = 0.618.$$

According to Fig. 16, this value of E_1 corresponds to an overflow acid of 60 per cent. Since the assumed value for the fraction of inlet oxides absorbed on the bottom plate leads to a gas-phase composition (N_1 , x_1 , and y_1), which is in equilibrium with the finished overflow acid, this is the correct absorption for a perfect plate under the specified conditions, within the limits of the accuracy of the fundamental data.

The heat generated per hour on the bottom plate may be computed from Eq. (13.62) by substituting the appropriate values for x , y , and f . It should be noted that $f_2 - z_2 = f_1 = 0.06$; hence, from Fig. 15, the HNO_3 overflowing from the second plate to the first plate must be 58.4 per cent. The average concentration on the bottom plate is 59.2 weight per cent. From Fig. 17 the apparent heat of formation of HNO_3 at this concentration is $-46,860$ C.h.u./lb. mole. This value is used in Eq. (13.62) to compute ΔH_1 ; hence

$$\frac{\Delta H_1}{1.192} = 0.06(-46,860 + 12,630) + 13,560(0.0539 + 0.036)$$

$$+ 6,850(0.0198 + 0.021),$$

$$\Delta H_1 = 1.192(-2,060 + 1,220 + 280) = -668 \text{ C.h.u./hr.}$$

That is, 668 C.h.u. are generated on the bottom plate per hour under the assumed operating conditions and must be removed at the same rate in order to hold the temperature at 45°C.

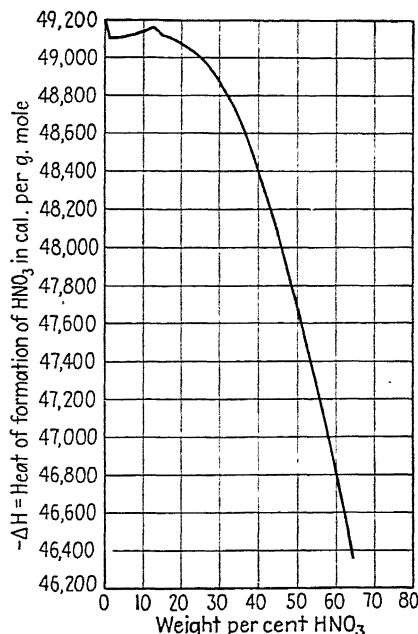


FIG. 17.—Apparent molar heat of formation of HNO_3 in aqueous solutions at 18°C.

PLATE 2.—The increase in oxidation of the gas between the surface of the liquor on plate 1 and the bottom of plate 2 may be estimated from Eq. (13.59). The constant C_5 is computed from the following values for the various constants appearing in C_5 :

$$P = 5 \text{ atm.}$$

$$N_0 = 0.07.$$

$$A = 0.197 \text{ sq. ft.}$$

$$R = 1.315 \text{ cu. ft. atm./deg. K.}$$

$$\Sigma_0 = 17.03.$$

At 45°C., k_B equals $2.46 \cdot 10^4$; therefore, k equals $6.5 \cdot 10^4$ and

$$C_5 = \frac{(125)(0.197)(6.5 \cdot 10^4)}{2(17.03)(0.07)(1.315)(318)} = 1,610.$$

Substituting this value in Eq. (13.59) gives

$$\frac{dx}{dh} = \frac{1.61 \cdot 10^3 N_i^2 (1 - x_i)^2}{(1 - f_i)(1 - 0.07f_i)} \{0.0918 - 0.07[f_i(1.5 - x_i) - (0.935 - x_i)]\};$$

substituting the above values for N_i , etc., gives

$$\left(\frac{dx}{dh}\right)_1 = 0.00705$$

for the rate of increase of the state of oxidation at the surface of the first plate. Consequently, the oxidation of the gas entering the vapor riser of the second plate (2 ft. above) is

$$x_2^e = 0.899 + 0.00705(2) = 0.913.$$

The calculations for plate 2 now proceed as in the case of the first plate:

$$\text{Guess } z_2 = 0.06, \quad f_2 = 0.12, \quad \text{and} \quad f_2 - z_2 = 0.06.$$

From Fig. 15, the overflow acid corresponding to $f_2 - z_2 = 0.06$ is 58.4 per cent. From Eq. (13.39),

$$x_2 = \frac{0.94(0.913) - 0.09}{0.88} = 0.874,$$

$$N_2 = \frac{0.07(0.88)}{0.992} = 0.0621,$$

$$B_2 = \frac{6.41 \cdot 10^{-2}}{(0.0621)(0.874)} = 1.182,$$

$$y_2 = \frac{3.182}{2} - \frac{1}{2}(10.12 - 4)^{1/2} = 0.353,$$

$$E_2 = \left(\frac{0.992}{0.88}\right)^2 \left(\frac{0.126}{0.181}\right) = 0.884.$$

Reference to Fig. 16 shows that the acid corresponding to this E is 58.3 per cent; consequently, the assumed value for z_2 is correct within the accuracy of these calculations. The heat liberated on the second plate, per hour, is

$$\begin{aligned} \frac{\Delta H_2}{1.192} &= (0.06)(-47,000 + 12,630) + 13,560(0.051 + 0.025) \\ &\quad + 6,850(0.0172 + 0.022), \\ \Delta H_2 &= 1.192(-772) = -920 \text{ C.h.u./hr.} \end{aligned}$$

The foregoing calculations serve to illustrate the method of handling problems of this sort. The final computations for the entire tower are recorded in Table 1. When desired, the individual NO , NO_2 , and N_2O_4 pressures in equilibrium with the acid leaving any given plate may be computed from the data in Table 1 and Eqs. (13.43) to (13.45).

TABLE 1.—THE ABSORPTION OF NITROGEN OXIDES IN ACID UNDER PRESSURE
(Temperature = 45°C. Pressure = 5 atm. abs. Finished acid = 60 wt. per cent)

| Plate | Mole fraction oxides gas leaving plate N_i | Oxidation x | | Association y gas leaving plate | Fraction inlet oxides absorbed i^{th} plate | Total fraction oxides absorbed | Weight per cent HNO_3 in overflow from i^{th} plate | Heat developed per hour, C.h.u. |
|-------|--|--------------------|-------------------|-----------------------------------|--|--------------------------------|---|---------------------------------|
| | | Gas entering plate | Gas leaving plate | | | | | |
| 1 | 0.0662 | 0.935 | 0.899 | 0.368 | 0.060 | 0.06 | 60.0 | 668 |
| 2 | 0.0621 | 0.913 | 0.874 | 0.353 | 0.060 | 0.12 | 58.4 | 920 |
| 3 | 0.0578 | 0.895 | 0.841 | 0.329 | 0.065 | 0.185 | 56.8 | 955 |
| 4 | 0.0525 | 0.873 | 0.805 | 0.310 | 0.080 | 0.265 | 55.0 | 1410 |
| 5 | 0.0456 | 0.848 | 0.747 | 0.281 | 0.100 | 0.365 | 52.1 | 1860 |
| 6 | 0.0378 | 0.806 | 0.653 | 0.228 | 0.115 | 0.480 | 48.6 | 2230 |
| 7 | 0.0300 | 0.745 | 0.542 | 0.175 | 0.110 | 0.590 | 43.7 | 2470 |
| 8 | 0.0235 | 0.650 | 0.409 | 0.115 | 0.090 | 0.680 | 38.2 | 2190 |
| 9 | 0.0192 | 0.545 | 0.324 | 0.085 | 0.060 | 0.740 | 33.5 | 1760 |
| 10 | 0.0163 | 0.467 | 0.278 | 0.060 | 0.040 | 0.780 | 30.0 | 1330 |
| 11 | 0.0141 | 0.414 | 0.242 | 0.045 | 0.030 | 0.81 | 27.2 | 1050 |
| 12* | 0.0124 | 0.370 | 0.214 | 0.040 | 0.023 | 0.833 | 26.0 | 820 |
| 13 | <0.0112 | 0.334 | <0.200 | 0.030 | >0.017 | >0.850 | >16.4 | 660 |

* Feed plate.

Examination of the data in Table 1 shows that, under the specified conditions of operations, 12 perfect plates should effect an absorption efficiency of 83.3 per cent. Since the overflow from this plate contains 26 per cent HNO_3 , the feed acid should be introduced onto this plate. Owing to the fact that the state of oxidation of the gas entering the top (13th) plate is still quite high (33.4 per cent), the fraction of oxides absorbed on this plate will exceed the required value of 0.017; therefore the over-all absorption efficiency for 13 perfect, isothermal plates would be

slightly greater than 85 per cent. The uncertainty is, however, less than the over-all accuracy of the calculations and is therefore unimportant.

It is interesting to note the course of the absorption as the gas passes up the tower. Only 6 per cent of the total inlet oxides are absorbed on the bottom plate; but, starting with the third plate, the fraction absorbed begins to increase and reaches a maximum on the sixth plate where 11.5 per cent of the total oxides are absorbed. After this the absorption work per plate begins to decrease quite rapidly and is only 3.0 per cent on the eleventh plate. As is to be expected, the heat generated on each plate practically parallels the absorption work per plate. The fact that the maximum heat development occurs on the seventh and not on the plate of maximum absorption is due to the fact that NO oxidation and NO₂ association also contribute to the total enthalpy change, in addition to the absorption of NO₂ and N₂O₄. The importance of adequate cooling facilities on the appropriate plates is clearly emphasized by these calculations. If, for example, all plates were uniformly provided with cooling coils capable of withdrawing about 1,000 C.h.u./hr., the temperatures on all plates would rise to such a point that the rate of heat generation would be equal to the capacity of the cooling coils to remove it. Since heat generation and absorption are roughly proportional, this means that the absorption performance would decline or, in other words, the unit would become inefficient both from the standpoint of maximum acid concentration producible, as well as over-all absorption efficiency.

In spite of the obvious shortcomings of the above type of analysis, valuable comparative data may be deduced regarding the effects of temperature, pressure, gas and liquor compositions, absorption efficiencies, plate spacings, etc. on the cost of producing nitric acids of various concentrations.

References

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2. SHERWOOD: "Absorption and Extraction," McGraw-Hill Book Company, Inc., New York, 1937.

CHAPTER XIV

AIR CONDITIONING

The necessity for adjusting the humidity and temperature of air to within certain definite limits is important in many process industries, in addition to the promotion of general living comfort. The essential principles constituting the basis for the design of equipment employed for this purpose are shown by the following illustration. In order not to obscure the underlying similarity of approach of this problem to those of gas absorption and converter design, the somewhat complex terminology of the air-conditioning industry will be avoided. The reader is referred to the text of Walker, Lewis, McAdams, and Gilliland¹ for a more complete discussion of the subject.

1. Design of Tower for Cooling and Dehumidifying Air.

Illustration.—Air containing 79 per cent relative humidity at 32°C. is to be cooled to saturated air at 19°C. in a 5-ft. diameter packed tower. The total quantity of moist air entering the tower per hour equals 29,690 lb. If 125 gal. of water per minute precooled to 15.3°C. are fed to the top of the tower, what would be the approximate height of tower required to effect the specified reduction in temperature, using countercurrent flows?

Solution.—If it is assumed that the heat leak through the walls of the tower to the surroundings is negligible, then, as will be shown, the problem is one of deriving a set of differential equations, which permit the evaluation of the net result of the following three rates of transfer, at any height h in the tower, when steady-state conditions have been established:

- a. The rate of transfer of H_2O from the gas to the liquid phase.
- b. The rate of transfer of sensible heat from the gas phase to the gas-liquid interface.
- c. The rate of transfer of heat from the gas-liquid interface to the bulk of the water.

The instantaneous rate of transfer of water from the gas to the liquid phase at any height h may be expressed analogously to the

rate of absorption of gases in liquids by the equation

$$dw = -Ka(P_{(g)} - P)dV, \quad (14.1)$$

where dw = pound moles water absorbed per hour by the element of packed volume dV at the height h .

$P_{(g)}$ = partial pressure H_2O in gas phase at h .

P = partial pressure H_2O from liquid phase, corresponding to the bulk liquid temperature t at the height h .

Ka = over-all coefficient of transfer, expressed as pound moles H_2O transferred from the gas to the liquid phase per hour per cubic foot per atmosphere H_2O .

The rate of transfer of sensible heat from the gas to the gas-liquid interface is

$$dQ = -h_{(g)}a(t_{(g)} - t_i)dV, \quad (14.2)$$

where dQ = C.h.u. transferred per hour from the gas to the interface in the element of volume dV .

$t_{(g)}$ = temperature of gas ($^{\circ}C.$) at the height h .

t_i = temperature ($^{\circ}C.$) at the gas-liquid interface.

$h_{(g)}a$ = gas film coefficient of thermal conductivity, expressed as C.h.u. per hour per cubic foot per degree centigrade temperature difference across film.

The rate of transfer of sensible heat from the gas-liquid interface to the bulk of the liquid is

$$dQ = -h_{(l)}a(t_i - t)dV, \quad (14.3)$$

where t = temperature of the bulk of the liquid, and $h_{(l)}a$ is the liquor film coefficient of heat conductivity in the same units as $h_{(g)}a$. Eliminating t_i from Eqs. (14.2) and (14.3) gives

$$dQ = -U_{(g)}a(t_{(g)} - t)dV, \quad (14.4)$$

where dQ = C.h.u. transferred per hour from the gas to the bulk of the liquid.

$U_{(g)}a$ = over-all coefficient of heat transfer in C.h.u. per hour per cubic foot per degree centigrade temperature difference.

Given the values of t° , $t_{(g)}^{\circ}$, $P_{(g)}^{\circ}$, P° and the quantity of air and water entering the tower per hour, it is possible to compute the values of t , $t_{(g)}$, $P_{(g)}$, and P at any height in the tower, and hence the required height, by the following procedure:

By assumption, the over-all process taking place in the tower is substantially one of constant enthalpy; therefore

$$H_0^\circ = H_0, \quad (14.5)$$

where H_0° = total enthalpy of materials entering tower per hour referred to 0°C. and liquid water as the zero level.

H_0 = total enthalpy of materials leaving tower per hour referred to 0°C.

Let W° = pound moles liquid H_2O entering tower per hour.

A = pound moles dry air entering tower per hour.

w° = pound moles gaseous water entering tower per hour.

t° = temperature entering water in $^\circ\text{C.}$

$t_{(g)}^\circ$ = temperature entering air.

ΔH_0 = heat of vaporization of 1 lb. mole H_2O at 0°C. in C.h.u.

In accordance with Eq. (14.5) the following equality may be set up:

$$18W^\circ t^\circ + (7A + 8w^\circ)t_{(g)}^\circ + w^\circ \Delta H_0 = 18Wt + (7A + 8w)t_{(g)} + w\Delta H_0, \quad (14.6)$$

where 7, 8, and 18 C.h.u./deg. C. have been used for the molar-heat capacities of air, water vapor, and liquid water, respectively. Differentiation of Eq. (14.6) yields

$$0 = 18Wdt + 18tdW + (7A + 8w)dt_{(g)} + 8t_{(g)}dw + \Delta H_0 dw. \quad (14.7)$$

But $dW = -dw$ and, therefore,

$$-18Wdt = (7A + 8w)dt_{(g)} + (8t_{(g)} - 18t + \Delta H_0)dw. \quad (14.8)$$

It can readily be shown that the factor $(8t_{(g)} - 18t + \Delta H_0)$ corresponds to ΔH , the heat of vaporization of the water, at the mean temperature of the gas and liquid at the height h ; therefore

$$-18Wdt = (7A + 8w)dt_{(g)} + \Delta H dw. \quad (14.9)$$

Equation (14.4) may be rewritten

$$(7A + 8w)dt_{(g)} = -U_{(g)}aS(t_{(g)} - t)dh, \quad (14.10)$$

where S is the cross-sectional area of the tower. Substituting for $dt_{(g)}$ from this equation and dw from Eq. (14.1) in (14.9) gives

$$-18Wdt = -U_{(g)}aS(t_{(g)} - t)dh - \Delta H(S)Ka(P_{(g)} - P)dh$$

or

$$\frac{dt}{dh} = \left(\frac{U_{(g)}aS}{18W} \right) (t_{(g)} - t) + \left[\frac{\Delta H(S)Ka}{18W} \right] (P_{(g)} - P). \quad (14.11)$$

From Eq. (14.10)

$$\frac{dt_{(g)}}{dh} = - \left(\frac{U_{(g)}aS}{7A + 8w} \right) (t_{(g)} - t) \quad (14.12)$$

and from (14.1)

$$\frac{dw}{dh} = -KaS(P_{(g)} - P). \quad (14.13)$$

The change of vapor pressure of the liquid water with temperature may be computed from the Clapeyron equation

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}, \quad (14.14)$$

where $T = t + 273.1$. Equations (14.11) to (14.14) constitute the required tools for computing t , $t_{(g)}$, $P_{(g)}$, and P at any height in the tower, since, when w is known, the partial pressure of H_2O in the air is given by the relation

$$P_{(g)} = \left(\frac{w}{A + w} \right) P_T, \quad (14.15)$$

where the total pressure P_T is assumed equal to 1 atm. By substituting for dt its value given by Eq. (14.11) and $T = 273.1 + t$ in the Clapeyron equation, it is possible to express P in terms of tower height. However, it will be found considerably easier to read P , corresponding to a given liquor temperature, from the $(P - t)$ plot, given on Fig. 18.

The coefficients of heat and mass transfer and other numerical values to be substituted in these equations are as follows:

$$Ka = 6.94 \text{ lb. moles } H_2O / (\text{hr.})(\text{cu. ft.})(\text{atm. } H_2O \text{ drive}).$$

$$U_{(g)}a = 35.0 \text{ C.h.u.} / (\text{hr.})(\text{cu. ft.})(\text{deg. C.}).$$

$$S = 19.6 \text{ sq. ft.}$$

$$\Delta H = 10,500 \text{ C.h.u.} / \text{lb. mole at } 25^\circ\text{C.}$$

$$W^\circ = (125 \cdot 8.35 \cdot 60) / 18 = 3,480 \text{ lb. moles } H_2O / \text{hr.}$$

$$A = 1,000 \text{ lb. moles dry air/hr.}$$

Substituting these values in Eqs. (14.11) to (14.13) gives the required working equations, (14.16) to (14.18). Under the

assumed conditions of operation the temperature of the liquor decreases with h , and therefore dt/dh must be inherently negative. Consequently,

$$\frac{dt}{dh} = -0.0109(t_{(g)} - t) - 22.8(P_{(g)} - P). \quad (14.16)$$

$$\frac{dt_{(g)}}{dh} = -0.0949(t_{(g)} - t). \quad (14.17)$$

$$\frac{dw}{dh} = -136(P_{(g)} - P). \quad (14.18)$$

Although the coefficients of the temperature and pressure terms in Eqs. (14.16) and (14.17) are not constants, they have been

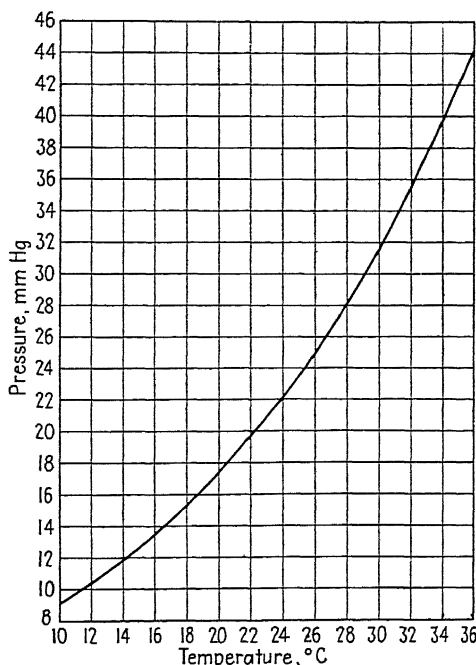


FIG. 18.—Vapor pressure of liquid water.

treated as such in this example. This is justified on the basis that the total liquor flow increases by a very small percentage from top to bottom and the contribution of the water vapor to the heat capacity of the gas ($7A + 8w$) is small. Therefore, the use of an average value for w introduces very little error.

The temperature of the water leaving the base of the tower may be estimated from Eq. (14.6), corresponding to the specified performance requirements for the unit. Thus the temperature of the water leaving the base of the tower is given by the equation

$$18(3,480)(15.3) + (7,000 + 306)(32) + 38.2(10,750) \\ = 18(3,496)(t) + (7,000 + 176)(19) + 22(10,750),$$

from which $t = 19.57^\circ\text{C}$.

The values of the three differential coefficients may be computed at the base of the tower from the following data:

$$t^\circ_{(0)} = 32^\circ\text{C}. \quad P^\circ = 0.0221 \text{ atm. (from Fig. 18).}$$

$$t^\circ = 19.57^\circ\text{C}. \quad w^\circ = 38.2 \text{ lb. moles.}$$

$$P^\circ_{(0)} = 0.0368 \text{ atm.}$$

$$\left(\frac{dt}{dh}\right)_0 = -0.0109(32 - 19.57) - 22.8(0.0368 - 0.0221), \\ = -0.1356 - 0.335 = -0.471.$$

$$\left(\frac{dt_{(0)}}{dh}\right)_0 = -0.0949(12.43) = -1.18.$$

$$\left(\frac{dw}{dh}\right)_0 = -136(0.0147) = -2.00.$$

At a distance of 1 ft. above the base these variables have the following values:

$$(t)_1 = 19.57 - 0.471(1) = 19.10^\circ\text{C}.$$

$$(t_{(0)})_1 = 32.0 - 1.18(1) = 30.82^\circ\text{C}.$$

$$w_1 = 38.2 - 2.00(1) = 36.2 \text{ lb. moles.}$$

$$(P_{(0)})_1 = \frac{36.2}{1,036} = 0.0349 \text{ atm.}$$

$$P_1 = 0.0215 \text{ atm. (from Fig. 18).}$$

The differential coefficients corresponding to these values of t_1 , w_1 , etc., are

$$\left(\frac{dt}{dh}\right)_1 = -0.0109(30.82 - 19.1) - 22.8(0.0349 - 0.0215), \\ = -0.128 - 0.306 = -0.434.$$

$$\left(\frac{dt_{(0)}}{dh}\right)_1 = -0.0949(11.72) = -1.11.$$

$$\left(\frac{dw}{dh}\right)_1 = -136(0.0134) = -1.82.$$

Therefore, at a distance of 2 ft. above the base,

$$(t)_2 = 19.10 - 0.434 = 18.67^\circ\text{C.}$$

$$(t_{(o)})_2 = 30.82 - 1.11 = 29.71^\circ\text{C.}$$

$$w_2 = 36.2 - 1.82 = 34.38 \text{ lb. moles.}$$

$$(P_{(o)})_2 = \frac{34.38}{1,034.4} = 0.0332 \text{ atm.}$$

$$P_2 = 0.0209 \text{ atm.}$$

Proceeding in the foregoing manner, the values recorded in Table 1 have been computed for the different variables, at the indicated heights above the base of the tower.

TABLE 1.—DESIGN OF PACKED TOWER FOR AIR CONDITIONING

| Interval | Height, ft. | Temperature, °C. | | <i>w</i> , lb. moles H ₂ O in gas | H ₂ O pressure, atm. | |
|----------|----------------|------------------|--------|--|---------------------------------|--------|
| | | Gas | Liquor | | Gas | Liquor |
| 0 | 0 | 32.0 | 19.57 | 38.2 | 0.0368 | 0.0221 |
| 1 | 1 | 30.82 | 19.10 | 36.2 | 0.0349 | 0.0215 |
| 2 | 2 | 29.71 | 18.67 | 34.38 | 0.0332 | 0.0209 |
| 3 | 4 | 27.60 | 17.87 | 31.04 | 0.0301 | 0.0200 |
| 4 | 6 | 25.76 | 17.20 | 28.30 | 0.0275 | 0.0192 |
| 5 | 8 | 24.14 | 16.64 | 26.04 | 0.0253 | 0.0186 |
| 6 | 10 | 22.72 | 16.17 | 24.22 | 0.0236 | 0.0180 |
| 7 | 12 | 21.48 | 15.77 | 22.70 | 0.0222 | 0.0176 |
| 8 | 14 | 20.40 | 15.44 | 21.45 | 0.0210 | 0.0172 |
| 9 | 16 | 19.46 | 15.16 | 20.42 | 0.0200 | 0.0168 |

According to the data recorded in Table 1, a tower approximately 17 ft. tall should meet the demands of the job. These calculations present a fundamentally correct method for estimating the size of equipment required for a definite air-conditioning performance, but it should be remembered that the accuracy of the answer is limited by the uncertainties in the numerical values of the over-all coefficients of mass and heat transfer. Furthermore, the assumption of no heat leak between the tower and the surroundings is obviously an oversimplification, which must be allowed for, either by greater cooling of the cooling water, or increased tower height. The limitations inherent in simple numerical integration of a system of simultaneous differential equations have already been discussed.

Reference

1. WALKER, LEWIS, McADAMS, and GILLILAND: "Principles of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1937.

CHAPTER XV

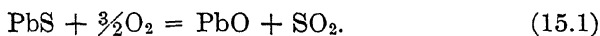
METALLURGICAL APPLICATIONS

The costliness of research and development work in the metallurgical industries makes this branch of technology one of the most fruitful fields for the applications of thermochemical principles. A few of the many types of problems that may advantageously be attacked with the aid of thermodynamics are illustrated in this chapter.

1. Roasting of Lead Ores. *Illustration 1.*—The roasting of galena (PbS), prior to the actual smelting operation, may result in the formation of the following substances, depending primarily on the concentrations of the gases in contact with the ore and the temperature: (1) PbO, (2) PbSO₄, (3) PbSO₄·PbO, and (4) Pb.

Investigate conditions of temperature and gas compositions favorable to the formation of each of these species from the equilibrium standpoint.

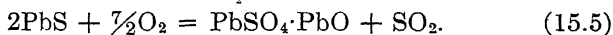
Solution.—The following set of reactions may be used to evaluate the possibility of forming the various substances by direct oxidation of PbS:



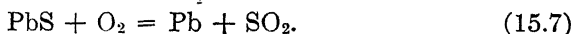
$$K_1 = \frac{P_{\text{so}_2}}{P_{\text{o}_2}^{3/2}}. \quad (15.2)$$



$$K_2 = \frac{1}{P_{\text{o}_2}^2}. \quad (15.4)$$



$$K_3 = \frac{P_{\text{so}_2}}{P_{\text{o}_2}^{7/2}}. \quad (15.6)$$



$$K_4 = \frac{P_{\text{so}_2}}{P_{\text{o}_2}}. \quad (15.8)$$



$$K_5 = \frac{P_{\text{so}_2}(\text{Pb})}{P_{\text{o}_2}}. \quad (15.10)$$

In Eq. (15.10) the factor (Pb) represents the activity of the molten lead, which is unity when the solubilities of the other components in it are assumed negligible.

The following standard free energy of formation equations are required:



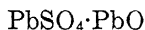
$$\Delta F^\circ = -70,635 + 1.04T \log T + 2.542 \cdot 10^{-3}T^2 + 8.4 \cdot 10^3T^{-1} - 7.16T. \quad (15.11)$$



$$\Delta F^\circ = -23,310 - 2.95T \log T + 2.12 \cdot 10^{-3}T^2 + 8.61T. \quad (15.12)$$



$$\Delta F^\circ = -216,380 + 16.51T \log T - 5.86 \cdot 10^{-3}T^2 - 1.877 \cdot 10^5T^{-1} + 39.36T. \quad (15.13)$$



$$\Delta F^\circ = -275,710 + 15.55T \log T - 6.38 \cdot 10^{-3}T^2 - 2.346 \cdot 10^5T^{-1} + 68.55T. \quad (15.14)$$



$$\Delta H_{298} = -51,990. \quad \Delta F^\circ_{298} = -45,100.$$

$$\Delta C_p = 0.425 + 1.03 \cdot 10^{-3}T + 0.939 \cdot 10^5T^{-2}. \quad (15.15)$$

$$\Delta H = -51,850 + 0.425T + 0.52 \cdot 10^{-3}T^2 - 0.939 \cdot 10^5T^{-1}. \quad (15.16)$$

$$\Delta F^\circ = -51,850 - 0.98T \log T - 0.52 \cdot 10^{-3}T^2 - 0.47 \cdot 10^5T^{-1} + 25.8T. \quad (15.17)$$



$$\text{Pb}_{(c)} = \text{Pb}_{(l)}. \quad (15.18)$$

$$\Delta F^\circ = 0, \quad \Delta H = 1,224 \text{ cal. at } 600.5^\circ\text{K.}$$

$$\Delta F^\circ = 1,224 - 2.04T. \quad (15.19)$$

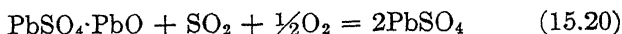
With the exception of Eqs. (15.15) to (15.19), all of the foregoing equations have been taken from Kelley's compilation of the thermodynamic properties of inorganic sulphur compounds.¹ The data used in deriving Eqs. (15.15) to (15.19) have also been taken from this source. These equations have been used to compute the free energies of formation of the various compounds

and the equilibrium constants of the reactions of interest at 527, 677, and 827°C. (see Table 1).

TABLE 1.—EQUILIBRIUM DATA FOR REACTIONS INVOLVED IN THE ROASTING OF GALENA

| | Temperature | | |
|---|----------------------|---------------------|---------------------|
| | 800°K. | 950°K. | 1100°K. |
| ΔF° SO ₂ | -72,300 | -72,200 | -71,960 |
| ΔF° PbS | -21,910 | -21,560 | -21,170 |
| ΔF° PbSO ₄ | -150,520 | -137,670 | -124,940 |
| ΔF° PbSO ₄ ·PbO | -189,100 | -172,610 | -156,040 |
| ΔF° PbO | -33,860 | -30,638 | -27,410 |
| K_1 | $10.0 \cdot 10^{22}$ | $5.0 \cdot 10^{18}$ | $3.4 \cdot 10^{15}$ |
| K_2 | $1.3 \cdot 10^{35}$ | $5.6 \cdot 10^{26}$ | $3.5 \cdot 10^{20}$ |
| K_3 | $3.2 \cdot 10^{59}$ | $2.5 \cdot 10^{46}$ | $7.9 \cdot 10^{36}$ |
| K_4 | $6.0 \cdot 10^{13}$ | $4.5 \cdot 10^{11}$ | $1.3 \cdot 10^{10}$ |
| K_5 | $7.6 \cdot 10^{13}$ | $6.6 \cdot 10^{11}$ | $2.0 \cdot 10^{10}$ |

Examination of the equilibrium constants recorded in Table 1 indicates that all of the foregoing reactions are thermodynamically possible between 800 and 1100°K. However, from the comparative magnitudes of the constants it is obvious that, if equilibrium is established, certain of the products would not appear in appreciable quantities in the roast. For example, the equation



represents the reaction between an acidic oxide and a basic oxide, and might be expected to go to practical completion. Thus, depending on the SO₂ and O₂ concentrations in the gas phase, any basic sulphate formed would go over to the ordinary sulphate.

At 1100°K., the equilibrium constant for reaction (15.20), computed from the above free-energy data, is $2.24 \cdot 10^4$; therefore

$$K_5 = \frac{1}{P_{\text{SO}_2} \cdot P_{\text{O}_2}^{1/2}} = 2.24 \cdot 10^4 \quad (15.21)$$

and

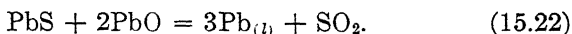
$$P_{\text{SO}_2} \cdot P_{\text{O}_2}^{1/2} = 4.46 \cdot 10^{-5}.$$

If $P_{\text{O}_2} = 0.21$ atm.; $P_{\text{SO}_2} = 9.75 \cdot 10^{-5}$ —and this represents the lowest pressure of SO₂ capable of converting basic sulphate

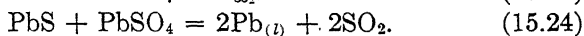
to PbSO_4 , in the presence of the normal O_2 concentration, at 1100°K . At lower temperatures the minimum SO_2 pressure required for conversion in the presence of 21 per cent O_2 would be still smaller.

Suppose now that the ore has been roasted with the amount of air theoretically required to convert the PbS to PbO , so that the SO_2 pressure equals 0.15 atm. In this case conversion of the basic to normal sulphate will occur if the O_2 pressure equals at least $8.8 \cdot 10^{-8}$ atm., at 1100°K . Thus it appears that the basic sulphate cannot exist under anything resembling equilibrium conditions, unless the ore is in contact with practically pure air or converter gases containing practically no oxygen.

Consider the two reactions



$$K_7 = P_{\text{so}_2}. \quad (15.23)$$



$$K_8 = P_{\text{so}_2}^2. \quad (15.25)$$

At 800°K ., K_7 and K_8 equal $4 \cdot 10^{-5}$ and $4.2 \cdot 10^{-8}$, respectively. Thus a partial pressure of $4 \cdot 10^{-5}$ atm. SO_2 in the roaster gases will stop reaction (15.22), and $2.05 \cdot 10^{-4}$ atm. of SO_2 will stop the reaction between the sulphide and the sulphate. However, at 1100°K ., K_7 and K_8 equal 0.642 and 0.93, respectively. Both reactions should go to completion since the SO_2 pressure cannot reach 0.64 atm. under ordinary operating conditions.

According to this analysis, it is theoretically possible to produce PbO , PbSO_4 , $\text{PbSO}_4 \cdot \text{PbO}$, and $\text{Pb}_{(l)}$ by direct oxidation of PbS with air, between 527 and 827°C . Owing to the thermodynamic properties of the substances involved, any basic sulphate formed is likely to be converted completely to the normal sulphate, unless the SO_2 and O_2 pressures fall below certain limits estimated in the foregoing discussion. It has also been found that at temperatures around 800°C . it is possible to roast directly to liquid lead, provided that there is available 1 mole of PbS to react with every 2 moles of PbO produced by roasting [Eq. (15.22)], and 1 mole of PbS for every mole of PbSO_4 produced by roasting [Eq. (15.24)]. However, since Eqs. (15.22) and (15.24) involve reactions between solid substances, they are probably much slower than the direct oxidation of PbS to PbO and PbSO_4 ; consequently, it would be very difficult to control the oxidation

to PbO and PbSO_4 so that the correct amount of PbS was left to react in accordance with Eqs. (15.22) and (15.24). It would therefore appear that PbO and PbSO_4 are the main products obtained in the roasting of galena.

2. Leaching Low-grade Ores to Recover Manganese.—A number of possible methods for recovering manganese from low-grade ores containing manganese carbonate (Chamberlain ores) have been discussed by Kelley.² The method based on the treatment of the ore with water and CO_2 under pressure is one of the more interesting methods, and is outlined as follows:

Illustration 2.—The nodules of Chamberlain ore have the following approximate composition:

| Constituent | Weight, Per Cent |
|--------------------------------|------------------|
| MnCO_3 | 32.9 |
| FeCO_3 | 23.0 |
| CaCO_3 | 28.6 |
| MgCO_3 | 3.3 |
| Al_2O_3 , etc. | 12.2 |

Consider a process in which

1. The ore is treated with sufficient water at a definite CO_2 pressure (P_{CO_2}), so that practically all of the MnCO_3 dissolves.

2. The saturated solution obtained in (1) is separated from the ore, while maintaining the CO_2 pressure at the value P_{CO_2} .

3. The CO_2 pressure over the solution is reduced to 1 atm., whereby the bulk of the MnCO_3 is caused to deposit, leaving the calcium, magnesium, and iron carbonates in solution.

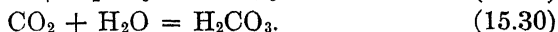
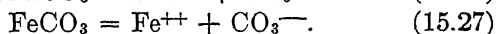
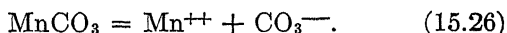
Compute:

a. The minimum amount of water required to dissolve all the CaCO_3 in 1 kg. of nodules under a CO_2 pressure of 1 atm.

b. The minimum CO_2 pressure (P_{CO_2}) required to dissolve all the accompanying MnCO_3 in this quantity of water.

c. The per cent of the original MnCO_3 deposited when the pressure is reduced from P_{CO_2} to 1 atm.

Solution.—a. The following equilibria are involved:



The corresponding equilibrium constants are

$$K_1 = (\text{Mn}^{++})(\text{CO}_3^{--}) = 5.05 \cdot 10^{-10}. \quad (15.31)$$

$$K_2 = (\text{Fe}^{++})(\text{CO}_3^{--}) = 2.11 \cdot 10^{-11}. \quad (15.32)$$

$$K_3 = (\text{Ca}^{++})(\text{CO}_3^{--}) = 4.82 \cdot 10^{-9}. \quad (15.33)$$

$$K_4 = \frac{(\text{HCO}_3^-)^2}{(\text{H}_2\text{CO}_3)(\text{CO}_3^{--})} = 8.1 \cdot 10^3. \quad (15.34)$$

$$K_5 = \frac{(\text{H}_2\text{CO}_3)}{f_{\text{co}_2}} = 0.0337. \quad (15.35)$$

The factors in parentheses represent activities; but, owing to the low solubilities of these compounds, ordinary molalities will be employed.

Numerical values of equilibrium constants are for 25°C. The solubility-product constants $K_1 - K_3$ have been taken from the afore-mentioned publication by Kelley², and K_5 and the following values for the ionization constants of H_2CO_3 have been taken from MacInnes:³

$$K_{\text{I}} = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = 4.52 \cdot 10^{-7},$$

$$K_{\text{II}} = \frac{(\text{CO}_3^{--})(\text{H}^+)}{(\text{HCO}_3^-)} = 5.59 \cdot 10^{-11}.$$

Since bicarbonate ion is very weakly ionized, it is reasonable to assume that substantially all the dissolved carbonate ion will be converted to bicarbonate ion, and (CO_3^{--}) may be replaced by (HCO_3^-) , K_4 , and K_5 . Equations (15.31) to (15.33) then become

$$\frac{(\text{Mn}^{++})(\text{HCO}_3^-)^2}{f_{\text{co}_2}} = K_1 K_4 K_5 = 1.38 \cdot 10^{-7}. \quad (15.36)$$

$$\frac{(\text{Fe}^{++})(\text{HCO}_3^-)^2}{f_{\text{co}_2}} = K_2 K_4 K_5 = 5.76 \cdot 10^{-9}. \quad (15.37)$$

$$\frac{(\text{Ca}^{++})(\text{HCO}_3^-)^2}{f_{\text{co}_2}} = K_3 K_4 K_5 = 1.32 \cdot 10^{-6}. \quad (15.38)$$

According to the foregoing analysis, 1 kg. of nodules contains 2.86 moles MnCO_3 , 1.98 moles FeCO_3 , 2.86 moles CaCO_3 , and 0.392 mole MgCO_3 . If x represents the number of kilograms of H_2O required to dissolve 2.86 moles of calcium when the CO_2 pressure equals 1 atm.; then

$$(\text{Ca}^{++}) = \frac{2.86}{x}.$$

$(\text{HCO}_3^-) = 2\Sigma m/x$, where Σm represents the moles $\text{Mn}^{++} + \text{Fe}^{++} + \text{Ca}^{++} + \text{Mg}^{++}$ per kilogram H_2O . The solubility of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is of the order of $3 \cdot 10^{-3}$ molal and, therefore, all the magnesium will dissolve. Thus the only three unknowns are the moles of $\text{Mn}^{++}(y)$, and $\text{Fe}^{++}(z)$, dissolved in x kg. of H_2O . Substituting in Eqs. (15.36) to (15.38) yields

$$\begin{aligned} \left(\frac{y}{x}\right) \left[\frac{2(2.86 + 0.392 + y + z)}{x} \right]^2 &= 1.38 \cdot 10^{-7}. \\ \left(\frac{z}{x}\right) \left[\frac{2(2.86 + 0.392 + y + z)}{x} \right]^2 &= 5.76 \cdot 10^{-9}. \\ \left(\frac{2.86}{x}\right) \left[\frac{2(2.86 + 0.392 + y + z)}{x} \right]^2 &= 1.32 \cdot 10^{-6}. \end{aligned}$$

Dividing the second equation by the third gives

$$z = \frac{(2.86)(5.76)}{1.32} \cdot 10^{-3} = 1.25 \cdot 10^{-2} = \text{moles Fe}^{++} \text{ in } x \text{ kg. of H}_2\text{O}.$$

Dividing the first equation by the second gives

$$y = \frac{(1.25 \cdot 10^{-2})(1.38 \cdot 10^2)}{5.76} = 0.299$$

= moles Mn^{++} in x kg. of H_2O .

Substituting these values in the third equation and solving for x give

$$x = 478 \text{ kg. H}_2\text{O required to dissolve all the calcium.}$$

b. In order to compute the CO_2 pressure required to dissolve 2.86 moles of Mn^{++} in 478 kg. H_2O , Eqs. (15.36) and (15.37) may be used

$$\begin{aligned} \frac{(6 \cdot 10^{-3})[2(6 \cdot 10^{-3} + 6 \cdot 10^{-3} + 8.2 \cdot 10^{-4} + m)]^2}{f_{\text{CO}_2}} &= 1.38 \cdot 10^{-7}. \\ \frac{(m)[2(6 \cdot 10^{-3} + 6 \cdot 10^{-3} + 8.2 \cdot 10^{-4} + m)]^2}{f_{\text{CO}_2}} &= 5.76 \cdot 10^{-9}. \end{aligned}$$

Dividing these two equations gives $m = 2.5 \cdot 10^{-4}$, or 0.119 mole of Fe^{++} will dissolve along with the manganese. f_{CO_2} may then be computed from either one of these equations, giving

$$f_{\text{CO}_2} = 29.7 \text{ atm.}$$

At 25°C., it is estimated from Fig. 3, Chap. V, that the activity coefficient of the CO_2 is about 82 per cent and, therefore, the actual CO_2 pressure is about 36 atm.

c. After the removal of the solution containing 2.86 moles MnCO_3 , 2.86 moles CaCO_3 , 0.39 mole MgCO_3 , and 0.119 mole of FeCO_3 (as bicarbonates) from the leached ore, and reducing the CO_2 pressure to 1 atm., the solubilities of manganese and iron will readjust to equilibrium with the reduced CO_2 pressure. In part (a) it was found that 478 kilos of H_2O dissolved 0.0125 mole of Fe^{++} and 0.299 mole of Mn^{++} under 1 atm. of CO_2 . Thus 2.56 moles of MnCO_3 containing 0.106 mole of FeCO_3 will deposit from this solution. The per cent recovery of the manganese contained in the original kilo of ore is, therefore, $100(2.56/2.86)$, or 89.5 per cent.

3. Purification of Zinc Concentrates.—The removal of lead and cadmium impurities from zinc concentrates, before or after roasting, has been the subject of a number of experimental and theoretical investigations. Maier⁴ has proposed a process based on the treatment of the unroasted zinc concentrate with H_2 for removing the cadmium sulphide. The process is analyzed from the thermal standpoint in the following illustration.

Illustration 3.—A zinc concentrate, having the following approximate composition, is to be treated with H_2 , for the purpose of removing cadmium and lead before roasting to the oxide:

| Constituent | Weight, Per Cent |
|-------------------------------|------------------|
| Zinc (ZnS)..... | 51.00 |
| Iron (FeS_2)..... | 2.79 |
| Lead (PbS)..... | 1.04 |
| Cadmium (CdS)..... | 0.56 |
| Sulphur..... | 31.00 |

Consider a purification process in which

1. The ore is heated in a slow stream of inert gas to 900°K. in order to decompose the iron pyrites.
2. The ore is heated in a slow stream of inert gas to 1200°K. in order to sublime the PbS .
3. Hydrogen is passed through the ore at 1200°K. in order to remove cadmium.

Compute a. the minimum quantity of inert gas required to decompose the iron pyrites at 900°K. per ton of ore.

b. The minimum quantity of inert gas required to sublime the PbS at 1200°K. per ton of ore.

c. The minimum quantity of H₂ required to remove the cadmium at 1200°K. per ton of ore.

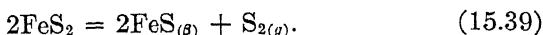
d. The total heat required (C.h.u.) in order to treat 1 ton of ore by this process.

Solution.—a. For the purpose of this analysis 1 ton of concentrate may be considered to consist of the following quantities of each component:

| | Pound Moles |
|------------------|-------------|
| FeS ₂ | 1.00 |
| PbS | 0.10 |
| CdS | 0.10 |
| ZnS | 18.9 |

The foregoing pound moles of ZnS are in excess of the actual zinc content of the ore but, since this figure is used only in estimating sensible heat requirements, the discrepancy is unimportant.

The heat of dissociation and dissociation pressure of pyrites at 900°K. may be computed from the following equations, given by Kelley,¹ for the reaction:



$$\Delta H = 63,500 + 10.45T - 10.18 \cdot 10^{-3}T^2. \quad (15.40)$$

$$\Delta F^\circ = 63,500 - 24.07T \log T + 10.18 \cdot 10^{-3}T^2 - 4.13T. \quad (15.41)$$

At 900°K.,

$$\Delta H = 64,660 \text{ cal.}$$

$\Delta F^\circ = 4,030$ cal.; therefore $K = 0.105$, and the dissociation pressure of pyrites is 0.105 atm. at 900°K. That is, P of $\text{S}_2 = 0.105$ atm., but there are also definite pressures of S_8 and S_6 in equilibrium with this pressure of S_2 . However, it may be shown on the basis of the known thermodynamic properties of S_8 and S_6 that the partial pressures of these more complex molecules are relatively unimportant under these conditions and may be neglected.

Since each pound mole of pyrites produces 0.5 lb. mole of S_2 , it is necessary to distill 0.5 lb. mole of S_2 from each ton of ore. The minimum lb. moles of inert gas, *e.g.*, nitrogen, corresponding to saturation of the inert gas with respect to S_2 would, therefore,

be

$$\text{Pound moles inerts} = 0.5 \left(\frac{0.895}{0.105} \right) = 4.26.$$

b. The minimum moles of inerts required to sublime 0.1 lb. mole of PbS from the ore may be computed when the vapor pressure of PbS is known at 1200°K. Kelley⁵ gives the following equations for the heat and free energy of vaporization of PbS:

$$\Delta H = 60,880 - 1.63T - 2.00 \cdot 10^{-3}T^2. \quad (15.42)$$

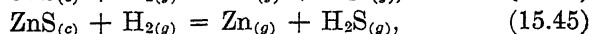
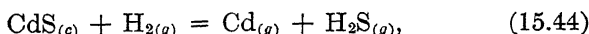
$$\Delta F^\circ = 60,880 + 3.75T \log T + 2.00 \cdot 10^{-3}T^2 - 54.62T. \quad (15.43)$$

At 1200°K., $\Delta F^\circ = 12,060$; therefore the vapor pressure of PbS equals $6.45 \cdot 10^{-3}$ atm. The minimum pound moles of inerts required to evaporate 0.1 lb. mole PbS from 1 ton of ore is given by the expression

$$\text{Pound mole inerts} = 0.10 \left(\frac{0.9936}{0.00645} \right) = 15.4.$$

c. The removal of cadmium by treatment with H_2 at 1200°K. depends on the reduction of the cadmium sulphide to the metal which has a vapor pressure greater than 1 atm., at this temperature.

The reactions to be considered are



for which

$$K_1 = \frac{P_{Cd} \cdot P_{H_2S}}{P_{H_2}}. \quad (15.46)$$

$$K_2 = \frac{P_{Zn} \cdot P_{H_2S}}{P_{H_2}}. \quad (15.47)$$

The free energies and heats of formations of the components of this system may be computed from the following equations, taken from the afore-mentioned compilations by Kelley:

CdS

$$\Delta H = -35,150 + 3.86T - 3.90 \cdot 10^{-3}T^2. \quad (15.48)$$

$$\Delta F^\circ = -35,150 - 8.89T \log T + 3.90 \cdot 10^{-3}T^2 + 26.40T. \quad (15.49)$$

$$\Delta H_{1200} = -36,130 \text{ cal.} \quad \Delta F^\circ_{1200} = -30,740 \text{ cal.}$$



$$\Delta H = -42,990 + 3.98T - 4.00 \cdot 10^{-3}T^2 + 1.946 \cdot 10^5 T^{-1}. \quad (15.50)$$

$$\Delta F^\circ = -42,990 - 9.17T \log T + 4.00 \cdot 10^{-3}T^2 + 0.973 \cdot 10^5 T^{-1} + 29.18T. \quad (15.51)$$

$$\Delta H_{1200} = -43,810 \text{ cal.} \quad \Delta F^\circ_{1200} = -36,050 \text{ cal.}$$



$$\Delta H = -3,725 - 3.05T - 1.865 \cdot 10^{-3}T^2. \quad (15.52)$$

$$\Delta F^\circ = -3,725 + 7.02T \log T + 1.865 \cdot 10^{-3}T^2 - 31.82T. \quad (15.53)$$

$$\Delta H_{1200} = -10,080 \text{ cal.} \quad \Delta F^\circ_{1200} = -13,340 \text{ cal.}$$



$$\Delta H = 27,010 - 0.49T - 1.233 \cdot 10^{-3}T^2. \quad (15.54)$$

$$\Delta F^\circ = 27,010 + 1.13T \log T + 1.233 \cdot 10^{-3}T^2 - 31.75T. \quad (15.55)$$

$$\Delta H_{1200} = 24,650 \text{ cal.} \quad \Delta F^\circ = -5,180 \text{ cal.}$$



$$\Delta H = 31,392 - 0.28T - 1.35 \cdot 10^{-3}T^2. \quad (15.56)$$

$$\Delta F^\circ = 31,392 + 0.64T \log T + 1.35 \cdot 10^{-3}T^2 - 31.17T. \quad (15.57)$$

$$\Delta H_{1200} = 29,110 \text{ cal.} \quad \Delta F^\circ = -1,700 \text{ cal.}$$

The standard free-energy changes for reactions (15.44) and (15.45) at 1200°K. are, therefore,

$$(15.44) \quad \Delta F^\circ = 12,220, \quad K_1 = 5.9 \cdot 10^{-3},$$

$$(15.45) \quad \Delta F^\circ = 21,010, \quad K_2 = 1.5 \cdot 10^{-4}.$$

If x = pound moles of H_2 introduced into the retort at 1200°K. and 1 atm. for the purpose of reducing the 0.10 pound mole of CdS to cadmium vapor, and if y = pound moles ZnS simultaneously reduced when the static system reaches equilibrium, then

$$K_1 = \frac{(0.1)(0.1 + y)}{(x + y + 0.1)(x - y - 0.1)} = 5.9 \cdot 10^{-3},$$

$$K_2 = \frac{y(0.1 + y)}{(x + y + 0.1)(x - y - 0.1)} = 1.5 \cdot 10^{-4}.$$

Solving these two equations gives $y = 2.55 \cdot 10^{-3}$ mole ZnS reduced, and $x = 1.33$ lb. moles of H_2 required. At 1 atm. and

1200°K. this corresponds to about 2,100 cu. ft. of H_2 . Since this quantity would obviously be too great to introduce all at once into the retort, it would be necessary to admit the H_2 at a very slow rate to the hot concentrate. If intimate contact of the finely divided concentrate and gas is ensured and the rate of gas passage is slow enough for the attainment of equilibrium, the actual quantity of hydrogen required for the removal of cadmium should not exceed this quantity by an undue amount.

Although the reduction of the FeS , present in the concentrate by means of H_2 , has been ignored in the foregoing discussion, it may readily be shown that the equilibrium ratios of H_2S , H_2 produced by cadmium and zinc reductions are so much greater than the H_2S/H_2 ratio in equilibrium with FeS that this substance cannot be reduced until the CdS has first been removed from the equilibrium system.

d. The principal enthalpy requirements for the treatment of 1 ton of ore by the above process may be estimated as follows:

1. Heat to raise 1 ton of ore from 298 to 900°K.:

$$\Delta H_1 = 20.1 \int_{298}^{900} (12.81 + 0.95 \cdot 10^{-3}T - 1.946 \cdot 10^5 T^{-2}) dT,$$

$$\Delta H_1 = 15.3 \cdot 10^4 \text{ C.h.u./ton.}$$

2. Heat to decompose 1 lb. mole FeS_2 at 900°K.:

$$\Delta H_2 = 63,500 + 10.45T - 10.18 \cdot 10^{-3}T^2, \quad (15.40)$$

$$\Delta H_2 = 6.47 \cdot 10^4 \text{ C.h.u./ton.}$$

3. Heat to raise 4.26 lb. moles N_2 from 298 to 900°K.:

$$\Delta H_3 = 4.26 \int_{298}^{900} (6.50 + 1 \cdot 10^{-3}T) dT,$$

$$\Delta H_3 = 1.82 \cdot 10^4 \text{ C.h.u./ton.}$$

4. Heat required to raise 1 ton of ore from 900 to 1200°K.:

$$\Delta H_4 = 20.1 \int_{900}^{1200} (12.81 + 0.95 \cdot 10^{-3}T - 1.946 \cdot 10^5 T^{-2}) dT$$

$$= 8.3 \cdot 10^4 \text{ C.h.u./ton.}$$

5. Heat required to sublime 0.1 lb. mole PbS at 1200°K.:

$$\Delta H_5 = 60,880 - 1.63T - 2.00 \cdot 10^{-3}T^2, \quad (15.42)$$

$$\Delta H_5 = 0.56 \cdot 10^4 \text{ C.h.u./ton.}$$

6. Heat required to raise 15.4 lb. moles N_2 , plus 1.33 pound moles H_2 from 298 to $1200^\circ K$.:

$$\Delta H_6 = 16.73 \int_{298}^{1200} (6.5 + 1.00 \cdot 10^{-3}T) dT,$$

$$\Delta H_6 = 10.92 \cdot 10^4 \text{ C.h.u./ton.}$$

7. Heat required to reduce 0.1 lb mole CdS to gaseous cadmium and H_2S at $1200^\circ K$.:

$$\Delta H_7 = -10,080 + 24,650 + 36,130 = 0.51 \cdot 10^4 \text{ C.h.u./ton.}$$

$$\text{Gross enthalpy requirement} = 4.39 \cdot 10^5 \text{ C.h.u./ton.}$$

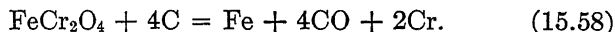
Part of the enthalpy added to this system may be recovered with suitable heat interchange equipment and used to preheat the nitrogen and hydrogen used in the process. Since the ore is at the approximate roasting temperature, no consideration need be given to the recovery of the sensible heat of the ore at $927^\circ C$. Assuming that a minimum temperature gradient of about $100^\circ C$. is maintained in the heat interchangers, then the following approximate quantities may be recovered:

$$\Delta H_3' = 1.82 \cdot 10^4 \times 50\%_{602} = 1.52 \cdot 10^4 \text{ C.h.u.}$$

$$\Delta H_6' = 10.92 \cdot 10^4 \times 80\%_{602} = 9.73 \cdot 10^4 \text{ C.h.u.}$$

Thus about $11.3 \cdot 10^4$ C.h.u./ton are recoverable, and the net enthalpy requirement = $3.26 \cdot 10^5$ C.h.u./ton of ore.

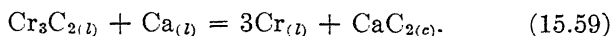
4. Decarburization of Ferrochrome with Calcium.—Chromium is usually produced by the reduction of chromite with carbon, in accordance with the equation



The impure product of the reduction, called ferrochrome, contains about 4 to 8 weight per cent carbon. Decarburization of this product may be effected by treatment with a fused mixture of lime, chromite, and fluorspar; and the use of calcium has also been proposed. Kelley⁶ has analyzed the latter method from the thermodynamic standpoint, as discussed in the following problem.

Illustration 4.—Assuming that the ferrochrome contains 6 per cent C, 65 per cent Cr, and 29 per cent Fe by weight, and that the carbon is combined in the form of Cr_3C_2 , compute the quantity of metallic calcium required per kilogram of ferrochrome to reduce the carbon content of the melt to 1 per cent at $1700^\circ K$, and calculate the composition of the equilibrium melt.

Solution.—The reaction that occurs in the melt is



The following free-energy data are required:

$$\begin{array}{c} \text{CaC}_2 \\ \Delta F^\circ = -13,210 + 6.9T \log T - 31.47T. \end{array} \quad (15.60)$$

$$\begin{array}{c} \text{Cr}_3\text{C}_{2(c)} \\ \Delta F^\circ = -8,550 - 5.03T. \end{array} \quad (15.61)$$

$$\begin{array}{l} \text{Cr}_3\text{C}_{2(c)} = \text{Cr}_3\text{C}_{2(l)} \quad \Delta H \approx 15,140 \text{ cal. at } 2163^\circ\text{K.} \\ \Delta F^\circ = 15,140 - 7T. \end{array} \quad (15.62)$$

$$\begin{array}{c} \text{Ca} \\ \text{Ca}_{(c)} = \text{Ca}_{(l)} \quad \Delta H = 2,230 \text{ cal. at } 1124^\circ\text{K.} \\ \Delta F^\circ = 2,230 - 1.98T. \end{array} \quad (15.63)$$

$$\begin{array}{c} \text{Cr} \\ \text{Cr}_{(c)} = \text{Cr}_{(l)} \quad \Delta H = 3,930 \text{ cal. at } 1823^\circ\text{K.} \\ \Delta F^\circ = 3,930 - 2.15T. \end{array} \quad (15.64)$$

The above data for the heat and free energy of fusion of Cr_3C_2 are very rough and are based on the assumption that the entropy of fusion of this compound equals seven units at the melting point. The free-energy change corresponding to reaction (15.59) at 1700°K. is, therefore,

$$\begin{aligned} \Delta F^\circ &= -28,810 + 840 + 1,140 + 13,860 = -12,970. \\ K_{1700} &= 46.2. \end{aligned}$$

Assuming that the activity coefficients in the melt are equal to unity, then

$$K = \frac{(N_{\text{Cr}})^3}{N_{\text{Ca}} \cdot N_{\text{Cr}_3\text{C}_2}}, \quad (15.65)$$

where the N 's represent mole fractions. In terms of moles 1 kg. of the ferrochrome initially contained 2.5 moles Cr_3C_2 , 5.0 moles Cr, and 5.2 moles Fe. If x and y represent the total moles of calcium added and the moles of calcium reacted, respectively, then

$$\begin{array}{ll} \text{Moles } \text{Cr}_3\text{C}_2 \text{ left in melt at equilibrium} &= 2.5 - y. \\ \text{Moles Ca left in melt at equilibrium} &= x - y. \\ \text{Moles Cr in melt at equilibrium} &= 3y + 5. \\ \text{Total moles in melt at equilibrium} &= 12.7 + x + y. \end{array}$$

Substituting the appropriate mole fractions in Eq. (15.65) gives

$$\frac{(3y + 5)^3}{(12.7 + x + y)(x - y)(2.5 - y)} = 46.2. \quad (15.66)$$

If 100P represents the weight per cent carbon left in the melt at equilibrium, then

$$P = \frac{2.5 - y}{41.7 - 2.67y + 1.67x}. \quad (15.67)$$

Equations (15.66) and (15.67) may be solved by trial and error for any desired extent of decarburization. Quantities appearing in these equations refer to the equilibrium melt produced by 1 kg. of the original ferrochrome. If it is desired to reduce the carbon content of the melt to 1 per cent, trial-and-error solution of these two equations gives $x = 5.0$ and $y = 2.05$ for the total moles of calcium required and the moles reacted. Thus the efficiency of utilization of the calcium would be about 41 per cent, and the melt would have the following composition, provided that the excess calcium were soluble in the melt:

| | Weight, Per Cent |
|----|------------------|
| C | 1.01 |
| Cr | 60.8 |
| Fe | 27.2 |
| Ca | 11.0 |

In view of the large excess of calcium required to drive the decarburization reaction to the right, the final product is quite impure. Although the thermodynamic data on which the above analysis is based are very rough, the conclusion that an undesirable excess of calcium is required for decarburization has been substantiated by experiments.

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CHAPTER XVI

LIQUEFACTION OF GASES

The constantly increasing use of liquefied gases for the production of low temperatures in various industrial chemical operations, and the large variety of liquefied gases available in cylinders are evidence of the commercial importance of this branch of applied thermodynamics. From the standpoint of pure science, it is obvious that the present high degree of development of the science of thermodynamics, from both the experimental and the theoretical sides, would have been impossible without the successful development of efficient processes for producing liquid air, hydrogen, and helium.

Depending on the nature of the gas to be liquefied, there are essentially five distinct methods, or principles, employed in the liquefaction of gases: (1) refrigeration; (2) compression; (3) adiabatic performance of work; (4) Joule-Thomson expansion; (5) magnetic cooling. Actually, most practical liquefaction processes involve combinations of two or more of these basic principles, as illustrated by the problems that follow.

1. Liquefaction by Refrigeration. *Illustration 1.*—From a mixture containing 88 per cent SO_2 , plus 12 per cent N_2 by volume, it is required to recover the SO_2 by cooling with brines refrigerated to $-33^\circ\text{C}.$, at 1 atm. pressure. Assuming the gases initially at $25^\circ\text{C}.$, estimate the minimum heat that must be withdrawn in order to produce 1 ton of liquid SO_2 , and estimate the over-all efficiency of SO_2 recovery by this process.

Solution.—The total heat to be removed is the sum of the sensible heat required to cool the original gas mixture from 25 to $-33^\circ\text{C}.$, plus the heat of liquefaction of 1 ton of SO_2 at this temperature.

The vapor pressure of liquid SO_2 at $-33^\circ\text{C}.$, as computed from the equation¹

$$\Delta F^\circ = -RT \ln p = 6,400 - 24.33T \quad (16.1)$$

is 0.313 atm. The minimum mole fraction of SO_2 in the gases

ordinary atmospheric temperatures, may be liquefied by simple compression without precooling. In estimating the amount of work required for liquefaction by this method, it is customary to assume that the process is carried out either isothermally or adiabatically.

2. Liquefaction by Compression. *Illustration 2.*—Estimate the minimum work required to liquefy 1 lb. mole of SO_2 by isothermal compression at 25°C ., and the total heat interchange required to produce 1 ton of liquid SO_2 at 25°C .

Solution.—*a.* According to the statement of the first law in the form [Eq. (2.1)]

$$(-dQ) = (-dW) + (-dE), \quad (16.3)$$

the heat to be withdrawn from the system ($-dQ$) equals ($-dW$)—the work done on the system, plus the decrease in the energy content of the system. The minimum work required for compression would be that involved in reversible, isothermal* compression, which equals the integral PdV , and the decrease in energy content may be computed from the relation (see L-R, p. 134)

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P. \quad (16.4)$$

The vapor pressure of SO_2 at 25°C ., as computed from the equation given in illustration 1, equals 4.26 atm. At these moderate pressures, the van der Waals equation may be employed with good accuracy to compute dE and dW . Thus,

$$\begin{aligned} -W &= -\int_{V_1}^{V_2} dW = -\int_{V_1}^{V_2} PdV \\ &= -\int_{V_1}^{V_2} \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV, \end{aligned} \quad (16.5)$$

which, when integrated, gives

$$-W = RT \ln \frac{V_1 - b}{V_2 - b} - a \left(\frac{1}{V_2} - \frac{1}{V_1} \right). \quad (16.6)$$

In this equation

$-W$ = work done on 1 g. mole SO_2 in compressing from the volume V_1 (at P_1 atm.) to the volume V_2 (at P_2 atm.).

b = 56.4 cc. for SO_2 .

a = $6.71 \cdot 10^6$ atm. cm.⁶ for SO_2 .

The molar volumes of SO_2 , computed from the van der Waals equation at 25°C ., are 24,250 cc. at 1 atm. and 5,500 cc. at 4.26 atm.; consequently

$$-W = 1,364 \log \frac{2.42 \cdot 10^4}{5.44 \cdot 10^3} - \frac{6.71 \cdot 10^6(1.987)}{82.06} (1.406 \cdot 10^{-4}).$$

$$-W = 885 - 22.8 = 862 \text{ C.h.u./lb. mole.}$$

This quantity represents the minimum work that must be done on 1 lb. mole of SO_2 in order to compress it to the liquefaction pressure at 25°C .

The decrease in internal energy may be calculated as follows: From the equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad (16.7)$$

it follows that

$$T \left(\frac{\partial P}{\partial T} \right)_v = \frac{RT}{V-b}$$

and

$$\left(\frac{\partial E}{\partial V} \right)_T = \frac{a}{V^2}. \quad (16.8)$$

Therefore

$$-\Delta E = - \int_{V_1}^{V_2} \frac{a}{V^2} dV = a \left(\frac{1}{V_2} - \frac{1}{V_1} \right). \quad (16.9)$$

Using the foregoing values for volumes and a ,

$$-\Delta E = 1.622 \cdot 10^5 (1.406 \cdot 10^{-4}) = 22.8 \text{ C.h.u./lb. mole.}$$

Thus it will be noted that the total heat to be removed per pound mole of SO_2 compressed equals $862 + 22.8 = 885$ C.h.u., of which the decrease in internal energy contributes only 2.57 per cent. It is also interesting to note that, if perfect gas behavior had been assumed, the heat of compression would be $1,364 \log 4.26 = 860$ C.h.u. The difference is less than the significant accuracy of the calculation, since the actual compression is neither isothermal nor reversible, and hence the total heat interchange will be greater than the computed value. The van der Waals value is, however, to be preferred, since it is larger than the perfect gas value.

The heat of vaporization of 6,400 C.h.u./lb. mole must be added to the heat of compression, giving 7,285 C.h.u. for the total heat

interchange involved in the production of 1 lb. mole of liquid SO_2 . The minimum heat to be removed per ton of liquid SO_2 is, therefore, $(31.2)(7,285) = 227,000$ C.h.u. Actually, the ΔH of vaporization should be corrected in order to allow for constant-pressure condensation at 4.26 atm. and 25°C ., instead of 1 atm. and -10°C . The correction is, however, a minor one and may be neglected in this case.

3. Cooling Produced by Adiabatic Performance of Work.

Illustration 3.—Assuming that nitrogen conforms to the van der Waals equation of state, estimate the temperature drop accompanying the adiabatic performance of work, when N_2 expands from 100 atm. pressure at 25°C . to 1 atm. pressure. The van der Waals constants for N_2 are $b = 38.5$ cc. and $a = 1.35 \cdot 10^6$ atm. cc.²

Solution.—According to the first law,

$$dE = dQ - PdV. \quad (16.10)$$

Since $dQ = 0$ for an adiabatic process, the work done by the system (PdV) corresponds to the decrease in energy content of the system. For a nonperfect gas the energy content is a function of T and V ; therefore

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV; \quad (16.11)$$

and, since $dE = -PdV$,

$$C_v dT + \left(\frac{\partial E}{\partial V}\right)_T dV = \left[\frac{-RT}{V-b} + \frac{a}{V^2}\right] dV. \quad (16.12)$$

In illustration 2, it was found that $\partial E/\partial V = a/V^2$ for a van der Waals gas; consequently

$$C_v dT + \frac{a}{V^2} dV = \frac{-RT}{V-b} dV + \frac{a}{V^2} dV,$$

or

$$C_v \frac{dT}{T} = -R \frac{dV}{V-b}. \quad (16.13)$$

Integrating between limits gives

$$\int_{298}^T C_v d \ln T = -R \int_{V_{100}}^{V_1} \frac{dV}{V-b}. \quad (16.14)$$

At temperatures below 298°K., C_v for N_2 is practically constant at the equipartition value for translation, plus rotation, *i.e.*, $\frac{5}{2}R$, hence

$$\frac{5}{2}R \log \frac{T}{298} = R \log \frac{V_{100} - b}{V_1 - b},$$

or

$$\left(\frac{T}{298}\right)^{5/2} = \frac{V_{100} - b}{V_1 - b}. \quad (16.15)$$

The equation

$$P = \frac{82.06T}{V - 38.5} - \frac{13.5 \cdot 10^5}{V^2} \quad (16.16)$$

may be used to compute the molar volume at 298°K. and 100 atm., but these two equations must be solved by trial and error in order to evaluate T and V .

At 298°K. and 100 atm., $V_{100} = 235$ cc.; if T is estimated to be 77°K., the molar volume of N_2 at this temperature would be 6,180 cc. Substituting these volumes in Eq. (16.15) gives $T = 75^\circ\text{K}$. Thus, if the gas conformed to van der Waals' equation all the way down to this temperature, and if the adiabatic work indicated by the right-hand side of Eq. (16.12) were performed, the gas would cool to the neighborhood of the boiling point of nitrogen. This is, of course, a rough calculation and is intended to give only an idea of the magnitude of the cooling to be expected by this method.

4. The Joule-Thomson Effect.—When a gas under pressure is forced through a porous plug or throttling valve, so that an appreciable pressure drop occurs across the restriction, the temperature of the gas on the two sides of the plug will differ when steady-state conditions prevail, provided that the system is substantially adiabatic. Since $Q = 0$, the first law equation

$$\Delta E = Q - \int dW \quad (16.17)$$

shows that the change in internal energy of the gas must be equal to the work done by it. Since no net external work is performed in operating some sort of an engine, the work done per mole of gas passing through the plug equals the difference between the work of expelling 1 mole of the gas from the low-pressure side of the plug, and the work done on the same quantity of gas in forcing it into the high-pressure side. The net work done by 1 mole

of the gas is, therefore,

$$W = P_2V_2 - P_1V_1, \quad (16.18)$$

where the subscripts 1 and 2 refer to conditions on the high- and low-pressure sides of the restriction, respectively. Substituting this value for W in Eq. (16.17) gives

$$E_2 - E_1 = -(P_2V_2 - P_1V_1),$$

or

$$E_2 + P_2V_2 = E_1 + P_1V_1. \quad (16.19)$$

Therefore

$$H_2 = H_1$$

or

$$\Delta H = 0. \quad (16.20)$$

That is, the Joule-Thomson expansion is an isenthalpic process.

As a quantitative measure of the behavior of gases in the Joule-Thomson expansion, it is customary to employ the coefficient defined by the equation

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H, \quad (16.21)$$

where μ represents the change in temperature per unit pressure drop. By means of standard thermodynamic relations (L-R, p. 134) this equation may be converted to the form

$$\mu = - \frac{(\partial H / \partial P)_T}{(\partial H / \partial T)_P} = \frac{T(\partial V / \partial T)_P - V}{C_p}. \quad (16.22)$$

Since for perfect gases $PV = RT$, it follows that $(\partial H / \partial P)_T$ is zero; consequently μ is always equal to zero for ideal gases. In other words, neither heating nor cooling would be observed in the free expansion of a perfect gas. It might therefore be anticipated that the temperature effects accompanying the Joule-Thomson expansion would increase with increasing deviations from ideality, and that the effect would be favored by low temperatures and high pressures. In a qualitative way, this has been confirmed by experiments. In accordance with Eq. (16.22), it should be possible to compute μ for any gas, under any set of conditions of temperature and pressure, when C_p and an equation of state valid in this region are available.

Except for problems of a mechanical nature, the most efficient operation of a Joule-Thomson liquefaction unit depends upon the

determination of operating pressures and temperatures at which the maximum fraction of the gas passing through the throttle valve can be liquefied. Obviously, the larger this fraction can be made, the smaller will be the amount of gas to be recycled and the smaller the compression work and size of equipment for a given rate of production. The principles involved in the determination of these optimum conditions are discussed in subsequent paragraphs.

Consider the passage of 1 mole of a gas A through a throttling valve under conditions such that a definite fraction F of 1 mole is condensed as liquid on the low-pressure side. The change of state is expressed by the equation

$$A_{(g)}(P_1, T_1) = FA_{(l)}(P_2, T_B) + (1 - F)A_{(g)}(P_2, T_2) \quad (16.23)$$

and, since $\Delta H = 0$,

$$H_1 = FH_{(l)} + (1 - F)H_2, \quad (16.24)$$

where H_1 = enthalpy of 1 mole of gas on the high-pressure side, *i.e.*, at the fore-pressure P_1 and the fore-temperature T_1 .

H_2 = enthalpy of 1 mole of gas at the effluent pressure P_2 and temperature T_2 .

$H_{(l)}$ = enthalpy of 1 mole of the liquid boiling at the temperature T_B , corresponding to the saturation pressure P_2 .

Solving Eq. (16.24) for F gives

$$F = \frac{H_2 - H_1}{H_2 - H_{(l)}} = \frac{(H_2 - H_{(l)}) - (H_1 - H_{(l)})}{H_2 - H_{(l)}}. \quad (16.25)$$

If the enthalpy of the liquid at the effluent pressure and temperature T_B is taken as the reference level for calculating enthalpies, then

$$F = \frac{H_2 - H_1}{H_2}. \quad (16.26)$$

The enthalpy of 1 mole of gas at the pressure P and temperature T referred to the zero point may be computed from the relation

$$H_0^{T,P} = \int_0^T C_p^\circ dT + \int_0^P \left(\frac{\partial H}{\partial P} \right)_T dP, \quad (16.27)$$

where C_p° represents the molar-heat capacity of the gas at 1 atmosphere pressure or less. The enthalpies in Eq. (16.26) are, therefore, expressed by the relations

$$H_2 = \int_0^{T_2} C_p^\circ dT + \int_0^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_2} dP - H_{(v)}, \quad (16.28)$$

$$H_1 = \int_0^{T_1} C_p^\circ dT + \int_0^{P_1} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP - H_{(v)}. \quad (16.29)$$

Substituting these two equations in (16.26) yields

$$F = \frac{1}{H_2} \int_{T_1}^{T_2} C_p^\circ dT + \frac{1}{H_2} \int_0^{P_2} \left(\frac{\partial H}{\partial P} \right)_{T_2} dP - \frac{1}{H_2} \int_0^{P_1} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP. \quad (16.30)$$

By substituting for $\partial H/\partial P$ in terms of (16.22) the following alternative form may be obtained:

$$F = \frac{1}{H_2} \int_{T_1}^{T_2} C_p^\circ dT - \frac{1}{H_2} \int_0^{P_2} (\mu C_p)_{T_2} dP + \frac{1}{H_2} \int_0^{P_1} (\mu C_p)_{T_1} dP. \quad (16.31)$$

Examination of these last two equations shows that the first integral on the right-hand side contributes a small term, which is roughly proportional to $T_2 - T_1$ and not sensitive to pressure. In fact, in a good liquefier the temperature of the effluent gas is elevated practically to the temperature of the inlet gas by means of efficient heat interchange; therefore, the first integral equals zero. For an ideal liquefier the fraction condensed as liquid may then be computed from the relation

$$F = - \frac{1}{H_2} \int_{P_1}^{P_2} (\mu C_p)_{T_1} dP = \frac{1}{H_2} \int_{P_1}^{P_2} \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right]_{T_1} dP. \quad (16.32)$$

The problem of determining the temperature and pressure at which F is a maximum is then a mathematical one, which may be solved when μ and C_p are known as functions of temperature, or when an accurate equation of state is available for substitution in the second integral of Eq. (16.32). The conditions for the

maximum are then determined by the usual method; that is,

$$\left(\frac{\partial F}{\partial T}\right)_P = 0 \quad \text{and} \quad \left(\frac{\partial F}{\partial P}\right)_T = 0. \quad (16.33)$$

In order to solve these equations mathematically, it is necessary that the equation of state be accurate over a wide enough range to include the conditions for the maximum. Since this is not usually the case, the more convenient procedure is to calculate F by graphical integration of Eq. (16.32) in a range of conditions dictated by such practical considerations as available fore-temperatures and pressures, and the inversion characteristics of the gas in question.

Referring to Eq. (16.22), it will be noticed that μ can be positive, zero, or negative, depending on whether $T(\partial V/\partial T)_P$ is greater, equal to, or less than V . Thus, depending on the pressure and temperature, the gas may cool or heat or show no temperature effect on expansion. The temperature and pressure at which the gas neither heats nor cools are called the inversion point. If, for simplicity, the gas is assumed to conform to the van der Waals equation of state, it can be shown^{2,p.71} by making the appropriate substitutions in the condition for inversion, *i.e.*,

$$T\left(\frac{\partial V}{\partial T}\right)_P - V = 0, \quad (16.34)$$

that for any pressure there are two temperatures satisfying this equation. In other words, for a given pressure there are upper and lower inversion temperatures at which the gas neither heats nor cools on expansion. Above the upper and below the lower inversion temperature, the gas heats when expanded; at temperatures in between the inversion points, the gas cools. In general, the choice of fore-temperatures is largely dictated by the cost of the refrigeration required to attain a certain degree of pre-cooling; consequently the fore-pressure should be chosen so that the already selected fore-temperature is not above the upper or below the lower inversion points corresponding to this pressure. Inversion temperatures or pressures may be estimated from the following correlation of the experimental data on inversion conditions, given by Jakob:³

$$P_r = 23.37 - 1.174\bar{R}T_r - \frac{178.6}{\bar{R}^2 T_r^2}. \quad (16.35)$$

In this equation P_r and T_r are the usual reduced pressure and temperature, respectively, and $\bar{R} = RT_c/P_cV_c$.

If, in addition to fixing the fore-temperature, the low-pressure side of the throttling valve is operated at 1 atm., then the only other condition remaining to be chosen is the fore-pressure. Referring to Eq. (16.32) for the fraction condensed in an ideal liquefier, it will be noticed that this equation may be rewritten

$$F = -k \int_1^{P_1} \left(\frac{\partial H}{\partial P} \right)_{T_1} dP = k \int_1^{P_1} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] dP, \quad (16.36)$$

where k is the reciprocal of the enthalpy of the effluent gas at 1 atm. and the fore-temperature. Differentiating this equation with respect to pressure and equating to zero show that for fixed fore-temperature the maximum fraction liquefied is obtained when

$$\frac{\partial F}{\partial P} = 0 = T \left(\frac{\partial V}{\partial T} \right)_P - V. \quad (16.37)$$

In other words, optimum operation is obtained when the fore-pressure corresponds to the inversion pressure for the chosen fore-temperature.

5. Calculation of Maximum Fraction of Hydrogen Liquefiable.

Illustration 4.—Assuming that H_2 precooled to the freezing point of nitrogen ($63.1^\circ K.$) is to be expanded to 1 atm. pressure in an ideal Joule-Thomson unit, estimate

a. The optimum fore-pressure to which the H_2 should be compressed.

b. The maximum fraction of the hydrogen liquefiable under these conditions of operation.

Solution.—a. Equation (16.35) may be used to estimate the inversion pressure corresponding to $63.1^\circ K.$ from the critical constants $T_c = 33.2^\circ K.$, $P_c = 12.8$ atm., and $R = 3.27$. Substituting these data in Eq. (16.35) gives the following equation for the inversion pressures of H_2 :

$$P_i = 299 - 1.48T - \frac{23.5 \cdot 10^4}{T^2}.$$

At $63^\circ K.$, P_i is computed to be 146 atm.

b. Equation (16.32) may now be used to estimate the maximum fraction liquefiable when hydrogen is expanded from 146 to

1 atm. To do this, available *PVT* data at low temperatures should be employed in order to integrate this equation graphically. However, for the purpose of estimating the fraction liquefied, the modified Beattie-Bridgman equation of state for hydrogen in the form

$$V = \frac{RT}{P} + \frac{\beta}{RT} + \frac{\gamma P}{R^2 T^2} + \frac{\delta}{R^3 T^3} P^2 \quad (16.38)$$

will be used. In this equation

$$\begin{aligned}\beta &= RTB_0 - A_0 - \frac{Rc}{T^2}, \\ \gamma &= -RTB_0b + A_0a - \frac{RB_0c}{T^2}, \\ \delta &= \frac{RB_0bc}{T^2},\end{aligned}$$

where $A_0 = 0.1975$.

$$a = -0.00506.$$

$$B_0 = 0.02096.$$

$$b = -0.04359.$$

$$c = 5.04 \cdot 10^2.$$

$$R = 0.08206.$$

Consequently, at 63.1°K.,

$$\beta = -0.0989.$$

$$\gamma = +0.00353.$$

$$\delta = -9.5 \cdot 10^{-6}.$$

Making the appropriate substitutions in Eq. (16.36) gives

$$F = \frac{1}{H_2} \int_1^{146} \left[B_0 - \frac{2\beta}{RT} + \frac{2c}{T^3} + \left(\frac{2B_0c}{T^3} - \frac{3\gamma}{RT} - B_0b \right) \frac{P}{RT} - \left(\frac{2B_0bc}{T^3} + \frac{4\delta}{RT} \right) \frac{P^2}{R^2 T^2} \right] dP.$$

Integration of this equation yields

$$F = \frac{1}{H_2} \left[\left(B_0 - \frac{2\beta}{RT} + \frac{2c}{T^3} \right) P + \left(\frac{2B_0c}{T^3} - \frac{3\gamma}{RT} - B_0b \right) \frac{P^2}{2RT} - \left(\frac{2B_0bc}{T^3} + \frac{4\delta}{RT} \right) \frac{P^3}{3R^2 T^2} \right]_1^{146}. \quad (16.39)$$

The quantity H_2 represents the enthalpy of 1 mole of hydrogen gas at 63.1°K. and 1 atm., referred to the enthalpy of 1 mole of

the liquid at the normal boiling point as zero. The heat of vaporization of hydrogen is 216 cal. at 20.4°K. (B-R); from Giauque's⁴ tabulation of the internal energy of gaseous hydrogen, it will be seen that the difference in internal energy of the 3:1 ortho-para mixture is negligible between these two temperatures. The difference between the enthalpy of 1 mole of the gas at 63.1°K. and at 20.4°K. is, therefore, $\frac{5}{2}R(63.1 - 20.4)$, or 212 cal. H_2 is, therefore, equal to 428 cal./mole, or 17.75 liter-atm. Substituting these data in Eq. (16.39) gives

$$F = \frac{1}{17.75} (9.14 - 2.21 + 0.427) = \frac{7.36}{17.75} = 0.414.$$

According to this calculation, the maximum fraction of the hydrogen liquefiable when the fore-temperature is 63.1°K. is 41.4 per cent. However, Keyes, Gerry, and Hicks,⁵ on the basis of some actual *PVT* data in this range, have computed a value of 30 per cent for the maximum fraction liquefiable under these conditions. This discrepancy emphasizes the importance of using actual *PVT* data corresponding to the conditions of interest, rather than extrapolated equation-of-state data. In general, the accuracy of equations of state near the critical region or at very low temperatures is not too good. If the Berthelot equation of state had been used, a value around 80 per cent would have been obtained for the maximum fraction liquefiable.

6. Estimation of Joule-Thomson Coefficients.—In certain cases where the net effect of free expansion involves only a cooling of the gas, it is possible to estimate Joule-Thomson coefficients from fugacity charts. According to Eq. (5.38), the change of fugacity with temperature at constant pressure is given by the relation

$$\left(\frac{\partial \ln f}{\partial T} \right)_P = \frac{H' - H}{RT^2}, \quad (5.38)$$

where $H' - H$ is the enthalpy change accompanying the vaporization of 1 mole of the substance from the pressure P to 1 atm., or less, at the temperature T .

If the change of state accompanying free expansion from the pressure P_1 to 1 atm. is represented by the scheme

$$A_{(g)}(P_1, T_1) = A_{(g)}(1, T_2), \quad (16.40)$$

then, since $\Delta H = 0$ for this process, it must also follow that $\Delta H = 0$ for the process in which the gas is expanded isothermally from P_1 to 1 atm., followed by cooling from T_1 to T_2 at 1 atm. pressure. The following equation is thereby obtained:

$$H(1, T_1) - H(P_1, T_1) + C_p(T_2 - T_1) = 0.$$

Since the enthalpy term $H(1, T_1)$ is to be identified with H' , it follows that

$$H' - H = C_p(T_1 - T_2). \quad (16.41)$$

It should be noted that $H' - H$ is the enthalpy change at the fore-temperature, and C_p is the heat capacity at the effluent (low) pressure.

Substitution of Eq. (16.41) in (5.38) yields

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{C_p(T_1 - T_2)}{RT^2}, \quad (16.42)$$

or

$$T_1 - T_2 = \frac{RT^2}{C_p} \left(\frac{\partial \ln f}{\partial T}\right)_P. \quad (16.43)$$

In using Eq. (16.43) to calculate the temperature drop accompanying expansion, T and P correspond to the fore-temperature and pressure T_1 and P_1 , and $(\partial \ln f / \partial T)_P$ must be evaluated from Fig. 3, Chap. V, at a temperature close to T_1 . That is, the change in $\ln f$ per degree absolute is required in the neighborhood of the fore-temperature at the pressure P_1 . This change is given approximately by the relation

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = \left(\frac{\Delta \ln f}{\Delta T}\right)_P = \left(\frac{2.3}{\Delta T} \log \frac{f_1}{f_2}\right)_{P_1}. \quad (16.44)$$

The approximate integral Joule-Thomson coefficient may then be computed from the relation

$$\mu = \frac{T_1 - T_2}{P_1 - 1}. \quad (16.45)$$

7. Magnetic Cooling.—This method is of great scientific interest since by means of it temperatures within a few thousandths of a degree of the absolute zero have been attained. In a rough, qualitative way the essence of the method is about as follows: When a magnetic substance is placed in a magnetic field

of strength \mathbf{H} , the magnetic dipoles, of which the substance is composed, undergo orientation in the field by an amount depending primarily on the ratio of the potential energy of the dipoles in the field to the thermal energy possessed by the dipoles. Obviously, the extent of orientation will increase with decreasing temperature, owing to the decreasing thermal energy of the dipoles. Since any process that substitutes a more ordered arrangement for a less ordered one is accompanied by a decrease in entropy, the substance liberates a definite amount of heat during the magnetization process. If this heat is absorbed by suitable interchange with a cooled body at T_0 , and if the magnetized body at T_0 is then transferred to a well-insulated evacuated container while maintaining the field constant, then no further temperature change will occur. If, now, the magnetic field is reduced to zero, the dipoles can once more revert to their former less ordered state of motion. However, since the system has been made adiabatic, the energy necessary to bring about this change must be derived from the internal energy of the substance; consequently, adiabatic demagnetization is accompanied by a drop in temperature.

The quantitative relationships involved are sketched below: The first law of thermodynamics modified to include the work done on the system by the action of the magnetic field is expressed by the equation

$$dQ = dE + PdV - \mathbf{H}d\mathbf{m}, \quad (16.46)$$

where \mathbf{m} is the component of the magnetization possessed by 1 mole of the substance in the direction of the magnetic field. The entropy increase accompanying a reversible change is, therefore,

$$dS = \frac{dE}{T} + P \frac{dV}{T} - \mathbf{H} \frac{d\mathbf{m}}{T}. \quad (16.47)$$

For a reversible, adiabatic process at zero pressure, $dS = 0$ and $P = 0$; therefore

$$\frac{dE}{T} = \frac{\mathbf{H}d\mathbf{m}}{T}. \quad (16.48)$$

Since adiabatic demagnetization is usually performed at very low temperatures ($< 0.7^\circ\text{K.}$) where the Debye third power law is valid,

$$dE = C_v dT = aT^3 dT;$$

consequently

$$\int_{T_0}^T aT^2 dT = \int_{T_0, \mathbf{H}_0}^{T, 0} \frac{\mathbf{H}}{T} d\mathbf{m}. \quad (16.49)$$

Integrating the left-hand side of this equation yields

$$T^3 = T_0^3 + \frac{3}{a} \int_{T_0, \mathbf{H}_0}^{T, 0} \frac{\mathbf{H}}{T} d\mathbf{m}. \quad (16.50)$$

In order to compute the temperature T , to which the system originally magnetized at T_0 will drop when the field \mathbf{H}_0 is removed, it is necessary to express \mathbf{m} as a function of \mathbf{H} and T before integrating Eq. (16.50). This has been done for certain idealized substances, but the results are so complicated that the papers of Giauque,⁶ Debye,⁷ and de Haas⁸ should be consulted for the details of the theoretical and experimental results. Thus far the lowest temperatures have been obtained by means of adiabatic demagnetization of mixed potassium, chromium, and aluminum alums.

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CHAPTER XVII

FLUID FLOW

In previous chapters an attempt has been made to present some of the types of problems encountered in plant design, which are amenable to thermodynamic analysis. Since most industrial chemical operations are carried out in flow systems, it is certainly true that the design of pipes, pumps, etc., required to introduce and withdraw the reactants and products from the system, is of equal importance to the design of the reaction vessel itself. A brief discussion of the fundamental principles involved in the flow of fluids and their application to a number of different problems are presented in this chapter.

The quantitative principles to be set forth may be employed in solving three principal types of problems: (1) estimation of power requirements for transferring fluids at specified rates of flow, (2) measurements of rates of flow, and (3) compression of fluids. For simplicity, only the flow of homogeneous liquids or gases, under steady-state conditions of operations, will be considered. No attempt will be made to treat sections of systems in which chemical changes are taking place, since the modifications in the procedure, required in order to allow for chemical energy effects, may be made on the basis of the principles discussed in preceding chapters.

1. The First Law of Thermodynamics for Flow Processes.—Owing to the fact that fluids in motion possess kinetic energy, as well as potential energy with respect to some conveniently chosen elevation, the first law of thermodynamics in the conventional nonflow form

$$\Delta E = Q - W \quad (17.1)$$

must be modified in order to include these forms of energy, in addition to the internal energy of the system. Furthermore, it will be found necessary to distinguish between the total external mechanical work the system does in running an engine, and the work required to introduce and expel any given quantity

of the fluid from the portion of the system under consideration—the flow work.

Thus the total energy brought into the fore-section of the apparatus by the unit mass of the flowing fluid is

$$E_1 + x_1 + \frac{U_1^2}{2g},$$

where E represents the internal energy, x the potential energy, and $U^2/2g$ the kinetic energy. Between the fore-section and the exit section, the unit mass of fluid absorbs Q units of heat from the surroundings and performs W_e units of external mechanical work. The total work performed by the fluid is, however,

$$W_T = W_e + P_2V_2 - P_1V_1, \quad (17.2)$$

where P_1V_1 represents the work done on the unit mass in forcing it into the apparatus at the pressure P_1 , and P_2V_2 is the work done by the same quantity on leaving the apparatus. The V 's represent specific volumes of the fluid at the two pressures.

The total energy carried out of the apparatus

$$E_2 + x_2 + \frac{U_2^2}{2g}$$

must, therefore, be equal to the total energy entering, plus the heat absorbed, minus the total work performed in the apparatus. Thus,

$$E_2 + x_2 + \frac{U_2^2}{2g} = E_1 + x_1 + \frac{U_1^2}{2g} + Q - (W_e + P_2V_2 - P_1V_1). \quad (17.3)$$

Hence

$$\Delta E + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) = Q - [W_e + \Delta(PV)] \quad (17.4).$$

or

$$\Delta E_T = Q - W_T, \quad (17.5)$$

where the subscripts indicate totals of all forms of energy or work involved in the flowing fluid between any two sections of the apparatus under analysis. The similarity of the flow form of the first law expressed by Eq. (17.5) to the nonflow form given by (17.1) is to be expected. Equation (17.4) may also be written

$$\Delta H + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) = Q - W_e, \quad (17.6)$$

where the enthalpy change has been substituted for $\Delta E + \Delta(PV)$. This equation readily leads to the previously derived equation for the Joule-Thomson expansion of a gas through an adiabatic throttling valve, by noting that Q , W_e , and $\Delta(x)$ are zero under the conditions of this process, and that $\Delta(U^2/2g)$ is insignificant; consequently

$$\Delta H = 0.$$

Referring to Eq. (17.2) it will be noted that the total reversible mechanical work performed—say, in expanding or compressing a gas—is W_T ; therefore,

$$W_T = \int_{V_1}^{V_2} P dV = W_e + \Delta(PV)$$

or

$$W_e = - \int_{P_1}^{P_2} V dP. \quad (17.7)$$

That is, in a flow process the net external, reversible mechanical work performed by the system is minus the integral VdP , whereas in a nonflow process it is the integral PdV . Expressed in different words, the net external, reversible work in a flow process equals the integral PdV , minus the flow work. In the Joule-Thomson expansion, flow work only is performed.

2. The Available Energy Balance for Flow Processes.—As a matter of experience, it is known that the mutual transformations of the various forms of energy and of heat into work in actual processes are accompanied by a degradation of energy into less useful forms. For this reason the foregoing statement of the first law—or the law of conservation of energy—is of less importance in practical applications than the statement of the available energy balance, known as Bernoulli's theorem. This equation may be derived from Eq. (17.3) as follows: Owing to the occurrence of irreversible processes in the flowing fluid, the actual energy possessed by the unit mass of the effluent fluid is not given by the left-hand member of Eq. (17.3), but contains a factor that represents the loss of energy per unit mass of flowing fluid due to friction. Thus Eq. (17.3) becomes

$$E_2 + x_2 + \frac{U_2^2}{2g} + F = E_1 + x_1 + \frac{U_1^2}{2g} + Q - (W_e + P_2 V_2 - P_1 V_1), \quad (17.8)$$

where F represents the energy loss due to flow friction between the two sections under consideration. Furthermore, although the fluid suffers a decrease in energy equal to W_e units, the actual energy W' delivered by an engine will be less than W_e , owing to the friction losses F' , occurring in the engine; consequently

$$W_e = W' + F'. \quad (17.9)$$

Equation (17.8) then becomes

$$\Delta E + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) + \Delta(PV) + \Sigma F - Q = -W', \quad (17.10)$$

where $\Sigma F = F + F'$.

If $\Delta E - Q$ is replaced by the equivalent reversible work for a nonflow process, operating between the same pressure-volume limits, the following equation is obtained:

$$-\int PdV + \Delta(PV) + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) + \Sigma F = -W' \quad (17.11)$$

or

$$\int VdP + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) + \Sigma F = -W'. \quad (17.12)$$

Equation (17.12) is usually referred to as Bernoulli's theorem. It should be noted that ΣF represents the total loss of energy (degraded energy) experienced by the unit mass of flowing fluid, owing to frictional causes between sections 1 and 2; and W' represents the net work actually delivered, per unit mass of fluid, by an engine actuated by the flowing fluid.

3. The Material Balance.—For the assumed conditions of steady flow, it is obvious that the quantity of matter passing any given section per unit of time must be equal to the quantity passing any other section per unit of time. Unless this statement were true, matter would tend to accumulate in some sections and to be exhausted in other sections. The material balance may be expressed by means of the equations

$$G_1A_1 = G_2A_2 = \dots = G_xA_x \quad (17.13)$$

or

$$\rho_1U_1A_1 = \rho_2U_2A_2 = \dots = \rho_xU_xA_x \quad (17.14)$$

or

$$\frac{U_1A_1}{V_1} = \frac{U_2A_2}{V_2} = \dots = \frac{U_xA_x}{V_x}. \quad (17.15)$$

In these equations the G 's represent mass velocities, the A 's cross-sectional areas, the ρ 's densities, the U 's average linear velocities, and the V 's specific volumes.

4. The Friction Equation.—Since thermodynamics is powerless to treat irreversible phenomena which are in any way dependent on rate factors, it is necessary to resort to various empirical correlations of experimental data in order to evaluate the friction loss (F) due to irreversible flow phenomena. By means of dimensional analysis, it may be shown (see Walker, Lewis, McAdams, and Gilliland, p. 75)¹ that, for steady flow in circular sections,

$$dF = 2f \left(\frac{U^2}{g} \right) \frac{dL}{D}, \quad (17.16)$$

where dL is a differential element of pipe length and

$$2f = \phi(DU\rho/\mu) = 2f\phi(R_e).$$

That is, the factor f is a function of the Reynolds number, which is defined by the relation

$$R_e = \frac{DU\rho}{\mu}, \quad (17.17)$$

where D and μ represent the pipe diameter and fluid viscosity, respectively. Since the Reynolds number is a dimensionless group, any self-consistent set of units may be used to evaluate this quantity.

A plot of the logarithm of the experimentally determined values of f vs. the logarithm of R_e gives two lines of distinctly different slopes, separated by a more or less indefinite region between Reynolds' numbers, 1,200 to 2,100. Visual observations indicate that below a Reynolds number of 1,200 the flow is essentially streamlined or viscous, and above 2,100 the flow is turbulent. The region between 1,200 and 2,100 is a transition or critical region. In the viscous region the function f has been experimentally found to be equal to $16/R_e$; consequently

$$dF = \frac{32\mu U}{\rho g D^2} dL. \quad (17.18)$$

That is, the energy loss per unit mass of fluid per unit length of pipe is proportional to the first power of the velocity and of the viscosity. This is the familiar Poiseuille's equation for capillary flow.

In the region of turbulent flow, f cannot be expressed as a simple function of R_e ; accordingly, the friction factor f corresponding to any specified flow conditions must be obtained from one of the standard plots of f vs. R_e . The value of F computed by this method may then be substituted in Bernoulli's equation in order to solve the given flow problem. It is still, however, necessary to make allowances for the engine friction losses F' in order to evaluate W' . Since F' , or the efficiency, is very often a well-known operating characteristic of a particular type of engine, Bernoulli's equation, as expressed by means of Eq. (17.12), is in suitable form for solving the given problem, in conjunction with the equations for the first law energy balance and the material balance.

The foregoing discussion of the method to be used for estimating flow friction losses has been confined to straight pipes of circular cross sections. A considerable body of correlated experimental data is available for estimating friction losses in noncircular flow sections, in bends, valves, and other types of fittings. These procedures are discussed in detail in the standard textbooks of chemical engineering.

5. Nonadiabatic Flow of Compressible Fluids. *Illustration 1.* Ethylene enters an unlagged section of horizontal pipe at a temperature of 427°C. , under a pressure of 50 atm. At a second section the temperature of the gas has fallen to 360°C. , but the pressure drop is negligible. The mass velocity of the ethylene is constant and equal to 80,000 lb./ (hr.) (sq. ft.). Compute the heat lost between the two sections per pound of ethylene.

Solution.—The heat lost to the surroundings may be computed from the first law energy balance, expressed by means of Eq. (17.6). In this case $\Delta(x)$ and W_e are zero, and Eq. (17.6) reduces to

$$Q = \Delta H + \Delta \left(\frac{U^2}{2g} \right). \quad (17.19)$$

The enthalpy change between sections 1 and 2 may be estimated as follows: The enthalpy of 1 lb. mole of C_2H_4 , at 360°C. and 50 atm., referred to the zero point is given by the equation

$$H_{633} = \int_0^{633} C_p^\circ dT + \int_1^{50} \left(\frac{\partial H}{\partial P} \right)_{633} dP, \quad (17.20)$$

where C_p° represents the molar-heat capacity at 1 atm. pressure or less. Similarly, the enthalpy at 427°C. and 50 atm. is given by the equation

$$H_{700} = \int_0^{700} C_p^\circ dT + \int_1^{50} \left(\frac{\partial H}{\partial P} \right)_{700} dP \quad (17.21)$$

and, therefore,

$$\Delta H = \int_{700}^{633} C_p^\circ dT + \int_1^{50} \left[\left(\frac{\partial H}{\partial P} \right)_{633} - \left(\frac{\partial H}{\partial P} \right)_{700} \right] dP. \quad (17.22)$$

In illustration 2, Chap. VII, the molar-heat capacity of C_2H_4 was computed and expressed by means of Eq. (7.64); consequently the first integral on the right side of (17.22) equals

$$\int_{700}^{633} (3.075 + 2.91 \cdot 10^{-2}T - 9.48 \cdot 10^{-6}T^2) dT = -1,230 \text{ C.h.u.}$$

The second integral may be estimated from Eq. (2.20), which is the integral of Eq. (2.18), using the Berthelot equation of state. The equation obtained for this integral is

$$\int_1^{50} \left[\left(\frac{\partial H}{\partial P} \right)_{633} - \left(\frac{\partial H}{\partial P} \right)_{700} \right] dP = \frac{162RT_c^3 \Delta P}{128P_c T_1^2 T_2^2} (T_2^2 - T_1^2), \quad (17.23)$$

where the critical temperature of C_2H_4 equals 282.8°K., and the critical pressure, 50.9 atm. Substitution of appropriate values in this equation yields -25.2 for the contribution of this integral to ΔH ; consequently

$$\Delta H(\text{total}) = -1,230 - 25.2 = -1,255 \text{ C.h.u.}$$

or

$$\Delta H \text{ per pound of } C_2H_4 = -44.8 \text{ C.h.u.}$$

Since the contribution of the second integral to the total enthalpy change is only 2.0 per cent, the error introduced by neglecting the effect of pressure on enthalpy would not be serious. However, where large temperature and pressure differences are involved, this factor cannot be ignored at elevated pressures.

The change in kinetic energy may be computed as follows: The mass velocity of the ethylene equals 80,000 lb./ (hr.) (sq. ft.); hence

$$80,000 = \rho_1 U_1 = \rho_2 U_2.$$

The densities of ethylene, under the specified conditions of temperature and pressure, may be estimated from the equation

$$\rho = \frac{28P}{C(1.315)(T)}, \quad (17.24)$$

where P equals the pressure in atmospheres, T equals degrees K, C is the compressibility factor, as read from Fig. 4, Chap. V, and ρ is the density in pounds per cubic foot.

The reduced pressure equals 0.998, and the initial and final reduced temperatures equal 2.47 and 2.24, respectively. Within the accuracy of compressibility charts, C is the same for these two temperatures; hence the difference in U is due to the temperature difference. Using a value of unity for C , gives $\rho_1 = 1.52$ and $\rho_2 = 1.68$ lb./cu. ft. The corresponding velocities are $U_1 = 14.6$ ft./sec. and $U_2 = 13.2$ ft./sec.; therefore

$$\Delta \left(\frac{U^2}{2g} \right) = \left(\frac{13.2^2}{64.3} \right) - \left(\frac{14.6^2}{64.3} \right) = -0.603 \text{ ft.-lb./lb.}$$

$$\text{or C.h.u. per pound} = - \frac{(0.603)}{(778)(1.8)} = -4.3 \cdot 10^{-4}.$$

Thus the total heat loss per pound of ethylene is

$$Q = -44.8 - 4.3 \cdot 10^{-4} = -44.8 \text{ C.h.u.}$$

These calculations illustrate the point that, unless the temperature and pressure drops are relatively large percentages of the inlet pressure and temperature, the contribution of the kinetic energy to the total heat loss is negligible.

6. Recovery of Work from Compressed Gases. *Illustration 2.*—It is required to recover the energy stored in a gaseous mixture, under a pressure of 10 atm., by expansion in a suitable engine, down to a pressure of 1 atm. The gas mixture contains chiefly 97 per cent N_2 , plus 3 per cent O_2 by volume. The compressed gases leave the top of an absorption column at 30°C. and 10 atm. pressure, at an elevation 45 ft. above the exhaust pipe (3.07 in. I.D.) of the engine. The mass velocity of the gas through the 1.05 in. I.D. pipe, connecting the absorption unit to the engine, equals 127,000 lb./(hr.)(sq. ft.). Assuming isothermal operation, compute (a) the maximum work theoretically recoverable per pound of gas passing through the engine; (b) the total heat that

must be absorbed from the surroundings in order to maintain isothermal conditions per pound of gas.

Solution.—*a.* Bernoulli's equation in the form

$$\int VdP + \Delta(x) + \Delta\left(\frac{U^2}{2g}\right) + F = -W_e \quad (17.25)$$

may be directly applied in this case. In the foregoing equation F represents the friction loss per pound of gas between the top of the absorption tower and the entrance to the expansion engine, and W_e represents the maximum work theoretically recoverable per pound of fluid in operating the engine. The actual work withdrawn from the engine shaft will, of course, be less by the friction losses in the engine itself.

Since at 10 atm. and 30°C. the compressibility factor of N_2 is but slightly greater than unity, the gaseous mixture will be treated as a perfect gas of molecular weight 28.11. At the top of the tower (section 1) $\rho_1 = 0.706$, and at the exhaust of the engine (section 2) $\rho_2 = 0.0706$ lb./cu. ft. The viscosity of air at this temperature is $1.8 \cdot 10^{-4}$ poise, which will be assumed as the value for N_2 under a pressure of 10 atm. The viscosity in English units, with time in hours, is therefore

$$(1.8 \cdot 10^{-4})(242) = 4.36 \cdot 10^{-2}.$$

The Reynolds number in the connecting pipe is

$$R_e = \frac{DG}{\mu} = \frac{(1.05)(127,000)}{(12)(4.36 \cdot 10^{-2})} = 255,000.$$

From the plot of f vs. R_e , on page 78 of Walker, Lewis, McAdams, and Gilliland,¹ the corresponding friction factor, f , to be substituted in Eq. (17.16) for computing the friction loss for flow through straight pipes, has the value 0.0045. Neglecting the loss in bends, the total loss of energy per pound of gas in the 45 ft. of vertical connecting pipe would be

$$F = 0.009 \left(\frac{U^2}{g} \right) \frac{45}{0.0875}$$

Equation (17.16) has been integrated in this case on the assumption that U does not change appreciably in the connecting pipe. From the specified mass velocity,

$$U_1 = \frac{127,000}{(0.706)(3,600)} = 50 \text{ ft./sec.}$$

and, therefore, $F = 360 \text{ ft. lb./lb. or } 0.257 \text{ C.h.u./lb.}$

The velocity in the exhaust pipe of the engine may be computed from the material balance in the form

$$\frac{127,000 A_1}{3,600} = 0.0706 U_2 A_2;$$

hence

$$U_2 = \frac{127,000}{(0.0706)(3,600)} \left(\frac{D_1}{D_2} \right)^2 = 58.5 \text{ ft./sec.}$$

Substituting the appropriate values in Eq. (17.25) yields

$$\begin{aligned} \frac{RT}{28.11} \int_{10}^1 \frac{dP}{P} - \frac{45}{1,400} + \frac{58.5^2 - 50^2}{(64.3)(1,400)} + 0.257 &= -W_e, \\ \frac{(4.575)(303)}{28.11} \log \frac{1}{10} - 0.0321 + 0.0102 + 0.257 &= -W_e, \\ -49.3 - 0.0321 + 0.0102 + 0.257 &= -W_e, \end{aligned}$$

or $W_e = 49.06 \text{ C.h.u.}$ theoretically recoverable per pound of gas by 100 per cent efficient expansion. It should be noted that the effect of the potential, kinetic, and frictional contributions on the sum, $-W_e$, is negligible compared to the VdP term in this particular instance.

b. The total heat that must be absorbed from the surroundings in order to maintain isothermal conditions may be computed from Eq. (17.6). Thus

$$Q = \Delta H + \Delta(x) + \Delta \left(\frac{U^2}{2g} \right) + W_e.$$

Since the process is assumed to be isothermal, the enthalpy difference is given by the term

$$\int_{10}^1 \left(\frac{\partial H}{\partial P} \right)_{303} dP,$$

which may be approximated by Eq. (2.20), if the Berthelot equation of state is assumed for nitrogen; therefore

$$\Delta H = \frac{9RT_c}{128P_c} \left(1 - 18 \frac{T_c^2}{T^2} \right) (1 - 10).$$

Substituting $T_c = 126.1$, $P_c = 33.5$, and $T = 303^\circ$ gives

$$\Delta H = 10 \text{ C.h.u./lb. mole, or } 0.356 \text{ C.h.u./lb.}$$

The total heat absorbed is, therefore,

$$Q = 0.356 - 0.0321 + 0.0102 + 49.06 = 49.39 \text{ C.h.u./lb. of gas.}$$

7. Flow of Gases Accompanied by Large Temperature Drop.

Illustration 3.—Air enters a 16-ft. length of a horizontal heat interchanger tube at 300°C. and 1.2 atm. pressure and leaves at 160°C. If the internal diameter of the tubing equals 1.05 in., and the mass velocity of the gas equals 15,000 lb./ (hr.) (sq. ft.), estimate the pressure drop in the tube.

Solution.—Substituting $W' = 0$, $\Delta(x) = 0$, and

$$dF = \left(\frac{2f}{D}\right) \left(\frac{U^2}{g}\right) dL$$

in Eq. (17.12) gives

$$\int V dP + \Delta \left(\frac{U^2}{2g}\right) + \int \frac{2f}{D} \left(\frac{U^2}{g}\right) dL = 0$$

or

$$V dP + \frac{U dU}{g} + \frac{2f U^2}{D g} dL = 0. \quad (17.26)$$

Since the mass velocity is constant and equal to U/V , where V is the specific volume, Eq. (17.26) becomes

$$V dP + \frac{G^2 V dV}{g} + 2f \frac{G^2 V^2}{D g} dL = 0$$

or

$$\frac{dP}{V} + \frac{G^2 dV}{g V} = -\frac{2f G^2}{D g} dL.$$

Substituting $V = RT/29P$ yields

$$29P dP + \frac{G^2 R T dV}{g V} = -\frac{2G^2}{D g} (RTf) dL. \quad (17.27)$$

Equation (17.27) contains four dependent variables: P , T , V , and f , which are functions of the independent variable L ; consequently this equation cannot be solved without making some simplifying assumptions. In the first place, it will be shown

that variations in f under the specified conditions may be neglected. The inlet Reynolds number is

$$R_e = \frac{DG}{\mu} = \frac{(0.0875)(15,000)}{(0.0726)} = 18,100$$

and the exit Reynolds number is

$$R_e = \frac{(0.0875)(15,000)}{(0.0605)} = 21,700.$$

Referring to the plot of f vs. R_e , mentioned in the preceding illustration, it will be found that the inlet and exit values of f are 0.0075 and 0.0072. In view of this minor change in f , the error introduced by using the constant value 0.0074 is negligible.

If the pressure drop through the tube is assumed to be small, then the change in V is largely determined by the temperature drop; therefore

$$\frac{dV}{V} = \frac{dT}{T}.$$

Furthermore, if the drop in temperature through the tube is assumed to be a linear function of the length of tube, then

$$T = 573 - 8.75L.$$

Substituting these simplifications in Eq. (17.27) gives

$$29PdP + \frac{G^2RdT}{g} = \frac{-2G^2R(0.0074)}{Dg} (573 - 8.75L)dL,$$

which, when integrated between limits, yields

$$\begin{aligned} 14.5(P_2^2 - P_1^2) + \frac{G^2R(T_2 - T_1)}{g} \\ = \frac{-2G^2R(0.0074)}{Dg} (573L - 4.38L^2). \quad (17.28) \end{aligned}$$

With P expressed in pounds per square foot, R equals 2,780 ft.-lb./lb. mole(deg. K.), g equals 32.17 ft./sec.², and G equals 4.16 lb./sec.(sq. ft.). Substitution of the specified values of P_1 , T_1 , T_2 , and L in this equation and solving give

$$P_2 = 2,510 \text{ lb./sq. ft.,}$$

or 1.186 atm. Thus it will be seen that the original assumption,

that the pressure drop through the tube is small, has been confirmed by these calculations.

The assumption that the air temperature decreases linearly with tube length is not too good. However, in view of the fact that the over-all pressure drop is small, uncertainties introduced by this assumption are not important. If a more precise solution were required, a second differential equation could be set up, expressing the over-all rate of transfer of heat from the air to the cooling medium surrounding the interchanger tube. These two equations could then be solved simultaneously by the numerical procedure employed in earlier chapters.

Reference

1. WALKER, LEWIS, McADAMS, and GILLILAND: "Principles of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1937.

APPENDIX 1

TABLE 1.—MOLAR-HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE
[Cal./ (mole)(deg.)]

| Gas | $C_p = a$ | + | bT | + | cT^2 | Range, °K. |
|------------------|-----------|---|-----------------------|---|-----------------------|-------------|
| H ₂ | 6.62 | | $0.81 \cdot 10^{-3}$ | | | 273 to 2500 |
| HCl | 6.70 | | $0.84 \cdot 10^{-3}$ | | | 273 to 2000 |
| HBr | 6.80 | | $0.84 \cdot 10^{-3}$ | | | 273 to 2000 |
| HI | 6.93 | | $0.83 \cdot 10^{-3}$ | | | 273 to 2000 |
| N ₂ | 6.76 | | $0.606 \cdot 10^{-3}$ | | $0.13 \cdot 10^{-6}$ | 300 to 2500 |
| O ₂ | 6.76 | | $0.606 \cdot 10^{-3}$ | | $0.13 \cdot 10^{-6}$ | 300 to 2500 |
| CO | 6.60 | | $1.2 \cdot 10^{-3}$ | | | 300 to 2500 |
| F ₂ | 6.50 | | $1.00 \cdot 10^{-3}$ | | | 300 to 3000 |
| Cl ₂ | 8.28 | | $0.56 \cdot 10^{-3}$ | | | 273 to 2000 |
| S ₂ | 7.75 | | $0.89 \cdot 10^{-3}$ | | | 300 to 1500 |
| SO | 6.99 | | $1.4 \cdot 10^{-3}$ | | | 300 to 1500 |
| CO ₂ | 7.70 | | $5.3 \cdot 10^{-3}$ | | $-0.83 \cdot 10^{-6}$ | 300 to 2500 |
| H ₂ O | 8.22 | | $0.15 \cdot 10^{-3}$ | | $1.34 \cdot 10^{-6}$ | 300 to 2500 |
| H ₂ O | 7.00 | | $2.77 \cdot 10^{-3}$ | | | 300 to 1500 |
| H ₂ S | 7.15 | | $3.32 \cdot 10^{-3}$ | | | 300 to 1800 |
| SO ₂ | 7.70 | | $5.30 \cdot 10^{-3}$ | | $-0.83 \cdot 10^{-6}$ | 300 to 2500 |
| NH ₃ | 6.70 | | $6.30 \cdot 10^{-3}$ | | | 300 to 800 |
| CH ₄ | 5.34 | | $11.5 \cdot 10^{-3}$ | | | 273 to 1200 |

TABLE 2.—MOLAR-HEAT CAPACITIES OF GASES AT CONSTANT PRESSURE
[Cal./ (mole)(deg.)]

| Gas | $C_p = a$ | + | bT | - | cT^{-2} | Range, °K. |
|-----------------|-----------|---|-----------------------|---|--------------------|-------------|
| NO | 8.05 | | $0.233 \cdot 10^{-3}$ | | $1.563 \cdot 10^5$ | 273 to 5000 |
| O ₂ | 8.27 | | $0.258 \cdot 10^{-3}$ | | $1.877 \cdot 10^5$ | 300 to 5000 |
| CO ₂ | 10.34 | | $2.74 \cdot 10^{-3}$ | | $1.955 \cdot 10^5$ | 273 to 1200 |
| CS ₂ | 13.75 | | $0.49 \cdot 10^{-3}$ | | $3.38 \cdot 10^5$ | 300 to 1800 |
| COS | 12.89 | | $0.83 \cdot 10^{-3}$ | | $3.60 \cdot 10^5$ | 300 to 1800 |
| HCN | 10.13 | | $2.08 \cdot 10^{-3}$ | | $2.49 \cdot 10^5$ | 400 to 1500 |
| SO ₂ | 11.4 | | $1.414 \cdot 10^{-3}$ | | $2.045 \cdot 10^5$ | 300 to 2500 |
| NH ₃ | 7.12 | | $6.09 \cdot 10^{-3}$ | | $0.398 \cdot 10^5$ | 300 to 1400 |
| CH ₄ | 6.73 | | $10.2 \cdot 10^{-3}$ | | $1.118 \cdot 10^5$ | 300 to 1200 |

TABLE 3.—MOLAR-HEAT CAPACITIES OF SOLIDS AT CONSTANT PRESSURE
[Cal./ (mole) (deg.)]

| Solid | $C_p = a$ | $+ bT$ | $- cT^{-2}$ | Range, °K. |
|--------------------------------|-----------|-----------------------|--------------------|-------------|
| AlCl ₃ | 13.25 | $28.0 \cdot 10^{-3}$ | | 273 to 466 |
| BaCO ₃ | 17.26 | $13.1 \cdot 10^{-3}$ | | 273 to 1083 |
| BaSO ₄ | 21.35 | $14.1 \cdot 10^{-3}$ | | 273 to 1323 |
| Bi ₂ O ₃ | 23.27 | $11.05 \cdot 10^{-3}$ | | 273 to 777 |
| CaO | 10.00 | $4.84 \cdot 10^{-3}$ | $1.08 \cdot 10^5$ | 273 to 1173 |
| CaCO ₃ | 19.68 | $11.89 \cdot 10^{-3}$ | $3.076 \cdot 10^5$ | 273 to 1033 |
| CaSO ₄ | 18.52 | $21.97 \cdot 10^{-3}$ | $1.568 \cdot 10^5$ | 273 to 1373 |
| C (graph.) | 2.672 | $2.617 \cdot 10^{-3}$ | $1.169 \cdot 10^5$ | 273 to 1373 |
| CuO | 10.87 | $3.576 \cdot 10^{-3}$ | $1.506 \cdot 10^5$ | 273 to 810 |
| FeO | 12.62 | $1.492 \cdot 10^{-3}$ | $0.762 \cdot 10^5$ | 273 to 1173 |
| PbCl ₂ | 15.88 | $8.35 \cdot 10^{-3}$ | | 273 to 771 |
| MgO | 10.86 | $1.197 \cdot 10^{-3}$ | $2.087 \cdot 10^5$ | 273 to 2073 |
| NiS | 9.25 | $6.40 \cdot 10^{-3}$ | | 273 to 597 |
| NH ₄ Cl | 9.80 | $36.8 \cdot 10^{-3}$ | | 273 to 458 |
| KCl | 10.93 | $3.76 \cdot 10^{-3}$ | | 273 to 1043 |
| KNO ₃ | 6.42 | $53.0 \cdot 10^{-3}$ | | 273 to 401 |
| Quartz (α) | 10.87 | $8.712 \cdot 10^{-3}$ | $2.412 \cdot 10^5$ | 273 to 848 |
| AgCl | 9.60 | $9.29 \cdot 10^{-3}$ | | 273 to 728 |
| NaCl | 10.79 | $4.2 \cdot 10^{-3}$ | | 273 to 1073 |
| ZnS | 12.81 | $0.95 \cdot 10^{-3}$ | $1.946 \cdot 10^5$ | 273 to 1173 |

NOTE: Data in Tables 1, 2, and 3 are taken from various summaries by K. K. Kelley referred to in text.

APPENDIX 2¹

EINSTEIN FUNCTIONS

TABLE E-1

$$C_v = 3RE(x) = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$

| x | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|-----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 0 | 5.961 | 5.953 | 5.941 | 5.917 | 5.882 | 5.838 | 5.785 | 5.723 | 5.653 | 5.574 |
| 1 | 5.488 | 5.395 | 5.294 | 5.188 | 5.076 | 4.959 | 4.837 | 4.711 | 4.582 | 4.450 |
| 2 | 4.316 | 4.180 | 4.043 | 3.906 | 3.768 | 3.630 | 3.493 | 3.356 | 3.222 | 3.089 |
| 3 | 2.958 | 2.830 | 2.704 | 2.581 | 2.460 | 2.344 | 2.231 | 2.121 | 2.015 | 1.912 |
| 4 | 1.813 | 1.717 | 1.625 | 1.538 | 1.452 | 1.371 | 1.293 | 1.219 | 1.149 | 1.082 |
| 5 | 1.018 | 0.957 | 0.899 | 0.844 | 0.792 | 0.744 | 0.697 | 0.653 | 0.611 | 0.572 |
| 6 | 0.536 | 0.500 | 0.466 | 0.436 | 0.407 | 0.379 | 0.354 | 0.330 | 0.307 | 0.286 |
| 7 | 0.266 | 0.248 | 0.231 | 0.215 | 0.200 | 0.185 | 0.172 | 0.160 | 0.149 | 0.138 |
| 8 | 0.128 | 0.119 | 0.110 | 0.102 | 0.0945 | 0.0884 | 0.0811 | 0.0752 | 0.0695 | 0.0650 |
| 9 | 0.0600 | 0.0554 | 0.0509 | 0.0468 | 0.0435 | 0.0400 | 0.0372 | 0.0340 | 0.0310 | 0.0286 |
| 10 | 0.0266 | 0.0247 | 0.0231 | 0.0212 | 0.0196 | 0.0180 | 0.0167 | 0.0152 | 0.0142 | 0.0129 |
| 11 | 0.0119 | 0.0110 | 0.0102 | 0.0093 | 0.0085 | 0.0078 | 0.0073 | 0.0067 | 0.0062 | 0.0057 |
| 12 | 0.0052 | 0.0048 | 0.0045 | 0.0041 | 0.0038 | 0.0035 | 0.0032 | 0.0029 | 0.0027 | 0.0024 |
| 13 | 0.0022 | 0.0020 | 0.0019 | 0.0017 | 0.0016 | 0.0015 | 0.0014 | 0.0013 | 0.0012 | 0.0011 |

¹ Tables given in Appendices 2 and 3 are reprinted by permission from "Thermodynamics and Chemistry" by MacDougall, published by John Wiley & Sons, Inc., New York.

APPENDIX 3

DEBYE FUNCTIONS

TABLE D-1

$$C_v = 3RD(x) = 9R \left(\frac{1}{X_D} \right)^3 \int_0^{X_D} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

| x | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0 | 5.961 | 5.96 | 5.95 | 5.94 | 5.92 | 5.89 | 5.86 | 5.82 | 5.78 | 5.74 |
| 1 | 5.676 | 5.62 | 5.55 | 5.49 | 5.42 | 5.35 | 5.27 | 5.19 | 5.10 | 5.01 |
| 2 | 4.919 | 4.83 | 4.74 | 4.65 | 4.55 | 4.44 | 4.34 | 4.24 | 4.14 | 4.04 |
| 3 | 3.945 | 3.84 | 3.74 | 3.65 | 3.55 | 3.45 | 3.36 | 3.27 | 3.18 | 3.09 |
| 4 | 2.999 | 2.91 | 2.83 | 2.75 | 2.67 | 2.59 | 2.51 | 2.43 | 2.35 | 2.27 |
| 5 | 2.200 | 2.13 | 2.06 | 2.00 | 1.94 | 1.88 | 1.82 | 1.76 | 1.70 | 1.64 |
| 6 | 1.583 | 1.53 | 1.48 | 1.43 | 1.38 | 1.34 | 1.30 | 1.26 | 1.22 | 1.18 |
| 7 | 1.138 | 1.103 | 1.068 | 1.034 | 1.001 | 0.969 | 0.938 | 0.908 | 0.880 | 0.854 |
| 8 | 0.831 | 0.811 | 0.791 | 0.771 | 0.751 | 0.732 | 0.713 | 0.694 | 0.675 | 0.656 |
| 9 | 0.637 | 0.618 | 0.599 | 0.580 | 0.561 | 0.542 | 0.524 | 0.506 | 0.487 | 0.469 |
| 10 | 0.451 | 0.435 | 0.421 | 0.409 | 0.398 | 0.388 | 0.378 | 0.368 | 0.359 | 0.351 |
| 11 | 0.343 | 0.335 | 0.327 | 0.319 | 0.311 | 0.303 | 0.295 | 0.287 | 0.280 | 0.273 |
| 12 | 0.267 | 0.261 | 0.255 | 0.249 | 0.243 | 0.237 | 0.231 | 0.225 | 0.220 | 0.215 |
| 13 | 0.210 | 0.205 | 0.200 | 0.196 | 0.192 | 0.188 | 0.184 | 0.180 | 0.176 | 0.172 |
| 14 | 0.168 | 0.164 | 0.161 | 0.158 | 0.155 | 0.152 | 0.149 | 0.146 | 0.143 | 0.140 |
| 15 | 0.137 | 0.134 | 0.131 | 0.128 | 0.125 | 0.123 | 0.121 | 0.119 | 0.117 | 0.115 |

| x | | x | | x | |
|-----|-------|-----|--------|-----|--------|
| 16 | 0.113 | 21 | 0.0499 | 26 | 0.0262 |
| 17 | 0.094 | 22 | 0.0433 | 27 | 0.0234 |
| 18 | 0.079 | 23 | 0.0380 | 28 | 0.0211 |
| 19 | 0.067 | 24 | 0.0335 | 29 | 0.0189 |
| 20 | 0.058 | 25 | 0.0296 | 30 | 0.0172 |

APPENDIX 4 ACTIVITY COEFFICIENTS OF VARIOUS TYPES OF ELECTROLYTES AS A FUNCTION OF MOLALITY

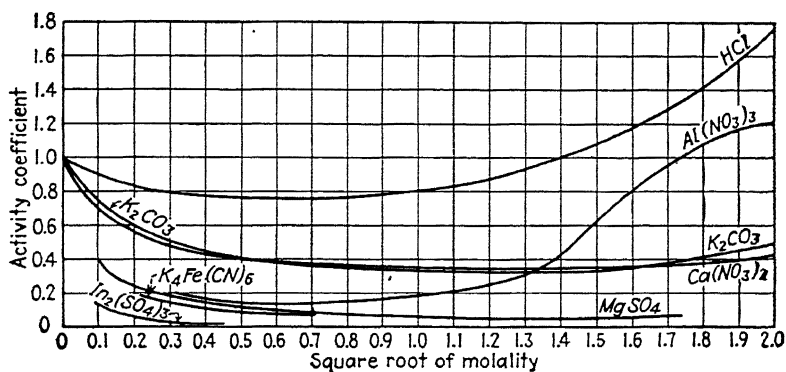


FIG. 19.—Activity coefficients of various types of electrolytes.

APPENDIX 5

TABLE 1.*—ENTROPIES OF AQUEOUS IONS AT 298.1°K.

[Cal./ (mole) (deg.)]

| Ion | $S^{\circ}_{298.1}$ | Ion | $S^{\circ}_{298.1}$ |
|--|---------------------|--|---------------------|
| H ⁺ | 0.00 | Hg ₂ ⁺⁺ | 17.7 ± 3 |
| Li ⁺ | 4.7 ± 1.0 | Sn ⁺⁺ | - 4.9 ± 1.0 |
| Na ⁺ | 14.0 ± 0.4 | Pb ⁺⁺ | 3.9 ± 0.9 |
| K ⁺ | 24.2 ± 0.2 | Al ⁺⁺⁺ | -76.0 ± 10 |
| Rb ⁺ | 28.7 ± 0.7 | Fe ⁺⁺⁺ | -61.0 ± 5 |
| Cs ⁺ | 31.8 ± 0.6 | Gd ⁺⁺⁺ | -32.5 ± 4† |
| Ag ⁺ | 17.54 ± 0.15 | OH ⁻ | -2.49 ± 0.06 |
| NH ₄ ⁺ | 26.4 ± 0.5 | F ⁻ | -2.3 ± 2 |
| Cl ⁻ | 13.5 ± 0.1 | IO ₃ ⁻ | 28.0 ± 1 |
| Br ⁻ | 19.7 ± 0.2 | HS ⁻ | 14.9 ± 1 |
| I ⁻ | 25.3 ± 0.5 | HSO ₃ ⁻ | 32.6 ± 1.5 |
| ClO ⁻ | 10.0 ± 2 | SO ₃ ⁻⁻⁻ | 3.0 ± 3 |
| ClO ₂ ⁻ | 24.1 ± 0.5 | HSO ₄ ⁻ | 30.6 ± 2 |
| ClO ₃ ⁻ | 39.4 ± 0.5 | SO ₄ ⁻⁻⁻ | 4.4 ± 1 |
| ClO ₄ ⁻ | 43.6 ± 0.5 | NO ₂ ⁻ | 29.9 ± 1 |
| BrO ₃ ⁻ | 38.5 ± 1.0 | NO ₃ ⁻ | 35.0 ± 0.2 |
| Tl ⁺ | 30.5 ± 0.4 | H ₂ PO ₄ ⁻ | 28.0 ± 1.5 |
| Ag(NH ₃) ₂ ⁺ | 57.8 ± 1.0 | HPO ₄ ⁻⁻⁻ | -2.3 ± 1.5 |
| Mg ⁺⁺ | -31.6 ± 3 | PO ₄ ⁻⁻⁻ | -45.0 ± 2 |
| Ca ⁺⁺ | -11.4 ± 0.3 | HCO ₃ ⁻ | 22.2 ± 0.8 |
| Sr ⁺⁺ | -7.3 ± 1.5 | CO ₃ ⁻⁻⁻ | -13.0 ± 1 |
| Ba ⁺⁺ | 2.3 ± 0.3 | C ₂ O ₄ ⁻⁻⁻ | 9.6 ± 1 |
| Fe ⁺⁺ | -25.9 ± 1.0 | CN ⁻ | 25 ± 5 |
| Cu ⁺⁺ | -26.5 ± 1.0 | MnO ₄ ⁻ | 46.7 ± 0.4 |
| Zn ⁺⁺ | -25.7 ± 1.0 | CrO ₄ ⁻⁻⁻ | 10.5 ± 1.0 |
| Cd ⁺⁺ | -16.4 ± 1.5 | | |

* LATIMER, PITZER, and SMITH: *J. Am. Chem. Soc.*, **60**, 1829 (1938).

† COULTER and LATIMER: *J. Am. Chem. Soc.*, **62**, 2557 (1940).

APPENDIX 6

TABLE 1.*—THE THERMODYNAMIC CONSTANTS FOR THE FORMATION OF SOME
GASEOUS HYDROCARBONS AT 298.1°K., REFERRED TO GRAPHITIC
CARBON AND HYDROGEN

| Substance | ΔS , cal./deg. | ΔH , cal./mole | ΔF° , cal./mole |
|---------------------------|---------------------------|---------------------------|---------------------------------|
| Methane..... | -19.39 | -17,865 | -12,085 |
| Ethane | -41.61 | -20,191 | -7,787 |
| Propane. | -64.4 | -24,750 | -5,550 |
| <i>n</i> -Butane..... | -87.5 | -29,715 | -3,630 |
| Isobutane..... | -91.2 | -31,350 | -4,160 |
| <i>n</i> -Pentane..... | -111.1 | -34,739 | -1,620 |
| 2-Methylbutane..... | -112.3 | -36,671 | -3,190 |
| Tetramethylmethane..... | -121.1 | -39,410 | -3,310 |
| <i>n</i> -Hexane..... | -134.5 | -40,010 | +80 |
| 2-Methylpentane..... | -136.8 | -41,800 | -1,000 |
| 2,2-Dimethylbutane..... | -141.2 | -44,400 | -2,300 |
| <i>n</i> -Heptane..... | -158.0 | -45,350 | +1,750 |
| 2-Methylhexane..... | -160.1 | -47,100 | +600 |
| 2,2-Dimethylpentane..... | -166.2 | -49,800 | -300 |
| <i>n</i> -Octane..... | -181.5 | -50,700 | +3,400 |
| 2,2,4-Trimethylpentane .. | -190.8 | -56,200 | +700 |
| Ethylene..... | -12.49 | +12,556 | +16,279 |
| Propylene..... | -32.8 | +4,956 | +14,730 |
| 1-Butene..... | -55.1 | +383 | +16,810 |
| cis-2-Butene | -56.9 | -1,388 | +15,570 |
| trans-2-Butene..... | -57.5 | -2,338 | +14,800 |
| Isobutene..... | -59.2 | -3,205 | +14,440 |
| Acetylene..... | +14.07 | +54,228 | +50,034 |

* PITZER: *Chem. Rev.*, **27**, 39 (1940).

APPENDIX 7

PROBLEMS

Problem 1. The Heat Capacity of Acetylene.—On the basis of the following assignment of fundamental vibration frequencies, compute the molar-heat capacity of $C_2H_{2(g)}$ at 300, 500, 700, 1000, 1300, and 1600°K.:

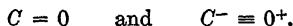
| Frequency, $cm.^{-1}$ | Degeneracy |
|-----------------------|------------|
| 612 | 2 |
| 729 | 2 |
| 1,973 | 1 |
| 3,283 | 1 |
| 3,372 | 1 |

From the computed values for C_p , deduce values for the constants a , b , and c in the equation

$$C_p = a + bT - cT^{-2}.$$

NOTE: Acetylene is a linear molecule.

Problem 2. The Entropy of Gaseous Carbon Monoxide.—Electron diffraction and thermal data indicate that the actual structure of the carbon monoxide molecule is a combination of the two resonance states expressed by the formulas



Assuming that the actual structure consists of 31 per cent double-bonded and 69 per cent triple-bonded states, compute the standard entropy of gaseous carbon monoxide at 25°C. and 1 atm. Values for covalent radii, given in Chap. IV, may be used. The fundamental vibration frequency of CO equals 2,167 $cm.^{-1}$. The computed value for $S^\circ_{298.1}$ should be compared with the rigorously computed value recorded in Chap. VIII.

Problem 3. The Entropy of Gaseous Acetylene.—On the basis of the frequency assignments given in Problem 1 and the covalent radii recorded in Chap. IV, compute the standard entropy of gaseous acetylene at 25°C. and 1 atm. pressure, and compare this value with the accepted value given in Chap. VIII.

Problem 4. Cooling by Joule-Thomson Expansion.—Estimate the temperature change accompanying the free expansion of propylene from an initial pressure of 50 atm. down to 1 atm. when the initial temperature is 200°C. The critical temperature of propylene equals 364.5°K., and the critical pressure 45.4 atm.

Problem 5. Theoretical Flame Temperature in the Combustion of Acetylene.—Assuming that acetylene is to be burned with the stoichiometric

amount of air, compute the maximum temperature that would be attained if the process were carried out adiabatically and if the reactants were preheated to 200°C.

NOTE: The heat capacity of $C_2H_{2(g)}$ has been computed in Problem 1.

Problem 6. The Heat Evolution Accompanying the Synthesis of HNO_3 from Nitrogen Oxides and Water.—Derive the following equation for the heat generated across each plate of a bubble-cap tower in which nitrogen oxides are being absorbed in HNO_3 :

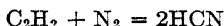
$$\frac{\Delta H}{n_0} = \Delta(f)(\Delta H_{HNO_3} + 12,630) + 13,560[\Delta(fx) - \Delta(x)] + 6,850[\Delta(xfy) - \Delta(xy)]. \quad (13.62)$$

See illustration 2, Chap. XIII, for the meaning of the various symbols.

Problem 7. The Absorption of Nitrogen Oxides in a Bubble-cap Column under 10 Atm. Pressure.—Using the data on gas compositions given in illustration 2, Chap. XIII, compute the number of perfect plates and the over-all height and diameter of a tower required to produce 10 tons of HNO_3 per day (as 60 weight per cent acid) at 10 atm. total pressure and 45°C., with an absorption efficiency of 95 per cent. Compute the heat that must be removed from each plate per hour in order to maintain the temperature of each plate at 45°C.

Assume a plate spacing of 18 in. and the same gas mass velocity used in Chap. XIII.

Problem 8. The Formation of HCN from Nitrogen and Acetylene.—Investigate the possibility of synthesizing HCN in accordance with the reaction



by computing the equilibrium conversions at 1 atm. and 200 atm. total pressure at 1000 and 1500°K. Assume an initially equimolar mixture of C_2H_2 and N_2 .

NOTE: The heat capacity of $C_2H_{2(g)}$ has been computed in Problem 1, and the following critical constants are available:

| | T_c , °K. | P_c , atm. |
|----------|-------------|--------------|
| C_2H_2 | 309 | 62 |
| N_2 | 126.1 | 33.5 |
| HCN | 456.7 | 50 |

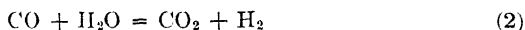
Problem 9. Hydrogen Cyanide from Carbon Monoxide and Ammonia.—The reaction



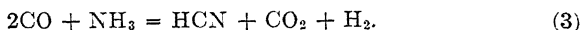
has been suggested as a means for producing HCN.

a. Using the necessary thermal data, compute the equilibrium fraction of NH_3 converted to HCN at 600, 700, and 800°K., starting with an initially equimolar mixture of CO and NH_3 at 1 atm. pressure.

b. Show that the reaction



is favorable at these temperatures; that, substantially, all the H_2O formed in (1) is removed by (2); and that the over-all reaction in this system will be



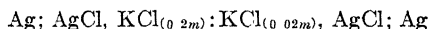
c. Compute the ammonia conversions at 600, 700, and 800°K. and 1 atm. pressure, starting with a mixture containing 2 moles of CO per mole of NH_3 .

Problem 10. Calculation of the Thermodynamic Constants of NH_4HS from Observed Dissociation Pressures.—The following values for the total equilibrium pressure over solid NH_4HS have been measured:

| Temperature, °K. | Pressure, atm. |
|------------------|----------------|
| 280.8 | 0.200 |
| 284.3 | 0.260 |
| 285.3 | 0.285 |
| 288.3 | 0.346 |
| 290.7 | 0.410 |
| 295.5 | 0.548 |
| 297.8 | 0.631 |
| 300.7 | 0.752 |

Compute the standard heat and free energy of formation and the entropy of $\text{NH}_4\text{HS}_{(c)}$ at 298.1°K.

Problem 11. The Electromotive Force and Temperature Coefficient of Concentration Cells with Transference.—Compute the electromotive force of the cell



at 25 and 35°C. from the following data:

a. Activity coefficient of 0.02*m* KCl at 25°C. = 0.869.

Activity coefficient of 0.20*m* KCl at 25°C. = 0.719.

b. Transference number of chloride ion = 0.51 at 25°C.

c. Bichowsky and Rossini give the following values for the $-\Delta H$ of formation of KCl in aqueous solutions at 18°C. (cal.):

| | |
|--|--------|
| $\text{KCl} \cdot \infty \text{H}_2\text{O}$ | 99,957 |
| $\text{KCl} \cdot 6400 \text{H}_2\text{O}$ | 99,924 |
| $\text{KCl} \cdot 3200 \text{H}_2\text{O}$ | 99,915 |
| $\text{KCl} \cdot 1600 \text{H}_2\text{O}$ | 99,906 |
| $\text{KCl} \cdot 800 \text{H}_2\text{O}$ | 99,899 |
| $\text{KCl} \cdot 400 \text{H}_2\text{O}$ | 99,899 |
| $\text{KCl} \cdot 200 \text{H}_2\text{O}$ | 99,912 |

Problem 12. The Synthesis of Ammonia from N_2 and H_2 .—Compute the volume per cent ammonia in the equilibrium mixture containing initially 3 moles of hydrogen per mole of nitrogen under the following conditions:

| Temperature, °K. | Total Pressure, atm. |
|------------------|----------------------|
| 700 | 200 |
| 800 | 200 |
| | 300 |
| 1000 | 100 |
| | 500 |

The critical constants of these gases are

| | T_c , °K. | P_c , atm. |
|-----------------|-------------|--------------|
| N ₂ | 126.1 | 33.5 |
| H ₂ | 33.3 | 12.8 |
| NH ₃ | 405.6 | 111.5 |

Problem 13. Heat Evolution Accompanying Dilution of Sulphuric Acid.—Compute the heat evolved at 18°C. when 50 per cent (weight) sulphuric acid is diluted with the appropriate quantity of water to produce a 10 per cent solution. Estimate the final temperature of the 10 per cent solution, if the dilution process were carried out adiabatically, assuming the acid and water initially at 18°C.

Problem 14. The Effect of Pressure on the Heat of Reaction.—Compute the heat of the reaction



at 298 and 1000°K. and 1 atm. pressure. Using the Berthelot equation of state, compute the heat of the reaction at these two temperatures under 200 atm. pressure. See Problems 1 and 8 for auxiliary data.

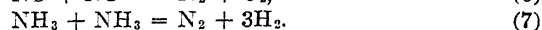
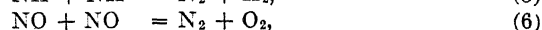
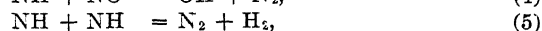
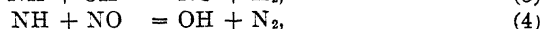
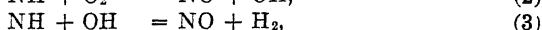
Problem 15. The Mechanism of Reactions Interpreted with the Aid of Thermodynamics.—The oxidation of ammonia with air in the presence of a catalyst is an important industrial reaction. Show that the reaction



constitutes a plausible primary step in the oxidation process by calculating the percentage dissociation of the NH₃ in accordance with this reaction at 1000°K. and 1 atm. pressure in a mixture containing 10 per cent NH₃ and 90 per cent air. The following data permit the evaluation of the thermodynamic constants of the NH molecule:

| | |
|---|--|
| Standard ΔH of formation | = 33,900 cal. |
| Fundamental vibration frequency | = 3,000 cm. ⁻¹ |
| Moment of inertia | = $1.694 \cdot 10^{-40}$ g. cm. ² |
| Weight of ground electronic level (³ Σ) | = 3. |
| Weight of upper electronic level (¹ Δ) | = 2. |
| Energy of upper level above ground | = 8,790 cm. ⁻¹ |

Estimate which of the following efficient and inefficient secondary reactions are thermodynamically possible at 1000°K.:



Discuss the effect of the usual kinetic factors on the permissible reactions.

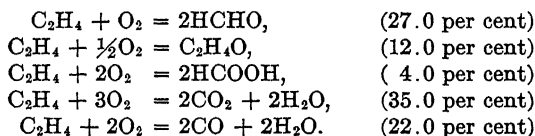
Problem 16. The Entropy of *n*-Heptane from Calorimetric Data.—On the basis of the following values for the molar-heat capacity compute the entropy of liquid *n*-heptane at 298.1°K.:

| Temperature, °K. | C_p , cal./deg. | Temperature, °K. | C_p , cal./deg. |
|------------------|-------------------|------------------|-------------------|
| 15.14 | 1 500 | 79 18 | 18.53 |
| 17.52 | 2.110 | 86.56 | 19.83 |
| 19.74 | 2.730 | 96.20 | 21.58 |
| 21.80 | 3.403 | 106.25 | 23.22 |
| 24.00 | 4.122 | 118.55 | 25.09 |
| 26.68 | 4.935 | 134.28 | 27.15 |
| 30.44 | 6.078 | 151.11 | 29.54 |
| 34.34 | 7.370 | 167.38 | 31.96 |
| 38.43 | 8.731 | 194.60 | 48.07 |
| 42.96 | 10.02 | 218.73 | 48.49 |
| 47.87 | 11.36 | 243.25 | 49.77 |
| 53.18 | 12.80 | 268.40 | 51.71 |
| 65.25 | 15.69 | 296.51 | 53.68 |
| 71.86 | 17 04 | | |

The molar heat of fusion equals 3,356 cal. at the melting point, 182.5°K.

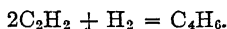
Problem 17. Cooling Accompanying Joule-Thomson Expansion of Nitrogen.—Estimate the drop in temperature accompanying the free expansion of nitrogen from 100 atm. down to 1 atm. when the initial temperature equals 25°C. The temperature drop accompanying the performance of flow work only should be compared with the drop accompanying the adiabatic performance of work computed in illustration 3, Chap. XVI.

Problem 18. The Temperature Rise Accompanying the Oxidation of Hydrocarbons.—A mixture of ethylene and air containing a mole fraction of ethylene equal to 0.029 is preheated to 300°C. before entering the reaction chamber. If the following reactions occur to the indicated extents, what would be the adiabatic temperature rise of the system?



NOTE: The heats of formation of the ethylene oxide, etc. are given in Bichowsky and Rossini; the heat capacity of C_2H_4 has been computed in Chap. VII; and the heat capacities of the other compounds may be estimated by the method of Bennewitz and Rossner, described in Chap. VIII.

Problem 19. Diolefins from Acetylene.—In connection with the production of synthetic rubber from butadiene, investigate the possibility of obtaining this compound by means of the reaction



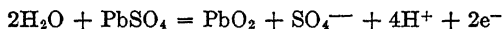
Discuss the conditions of temperature, pressure, and concentrations likely to be favorable to the formation of this compound and the possible unfavorable side reactions.

Problem 20. The Heat Capacities of KCl and H_2O in Aqueous Solutions. From the following observed specific heats at $25^\circ C.$ and $35^\circ C.$, compute the apparent molar-heat capacities of the KCl, the partial molar-heat capacities of the KCl, and the relative partial molar-heat capacities of the H_2O at the indicated concentrations:

| Molality of KCl | Specific Heat, cal./g. of solution | |
|-----------------|------------------------------------|---------------|
| | $25^\circ C.$ | $35^\circ C.$ |
| 0.010 | 0.9968 | 0.9964 |
| 0.050 | 0.9929 | 0.9927 |
| 0.070 | 0.9908 | 0.9906 |
| 0.100 | 0.9881 | 0.9880 |
| 0.300 | 0.9695 | 0.9699 |
| 0.699 | 0.9342 | 0.9351 |
| 1.027 | 0.9090 | 0.9105 |

Compute average values for the temperature coefficients of the three heat capacities in this range of temperatures and concentrations.

Problem 21. Single Electrode Potentials from Thermal Data.—Compute the standard potential of the half cell



at $25^\circ C.$, from heats of formation given in Bichowsky and Rossini and entropy data included in the text. Use 16.75 units for the entropy of liquid water. Compare this value with the value -1.685 volts given in Latimer's "Oxidation Potentials."

Problem 22. The Effect of Temperature on Compressibility Factors.—Show that the change of compressibility factor with temperature at constant pressure is related to the Joule-Thomson coefficient and the heat capacity at constant pressure by means of the equation

$$\left(\frac{\partial C}{\partial T}\right)_p = \frac{P\mu C_p}{RT^2}.$$

A mixture of methane and butane containing a mole fraction of methane equal to 0.970 has a compressibility factor of 0.9673 at 51 atm. pressure and 394.1°K. Using the following values for the Joule-Thomson coefficients and molar-heat capacities of the mixture, compute the compressibility factor at 294.2°K. and 51 atm.:

| Temperature, °K. | μ , °K./atm. | C_p , cal./°K. |
|------------------|------------------|------------------|
| 294.2 | 0.436 | 10.35 |
| 327.5 | 0.344 | 10.30 |
| 360.8 | 0.274 | 10.51 |
| 394.1 | 0.215 | 10.80 |

Problem 23. Hydrogenation of Hydrocarbons.—Isobutene may be polymerized to form diisobutene which in turn may be hydrogenated to produce *i*-octane. This compound is important in the manufacture of aviation gasoline. Assuming that *i*-octane, *i*-butene, and *i*-butane are the only compounds formed when gaseous diisobutene and hydrogen are passed over a nickel catalyst, compute the mole per cent diisobutene converted to each of these three products under the following operating conditions, when equilibrium is attained:

| Case | A | B | C | D | E |
|--|-----|-----|-----|------|-----|
| Temperature, °K..... | 350 | 450 | 350 | 350 | 350 |
| Total pressure, atm..... | 1 | 1 | 1 | 1 | 10 |
| Initial mole ratio diisobutene to H ₂ | 1 | 1 | 2 | 0.33 | 1 |

The following thermal data, based on the older data for CO₂, may be used (all compounds in gaseous state):

| | ΔH_{298} , cal. | ΔF°_{298} , cal. |
|--|-------------------------|-------------------------------|
| <i>i</i> -C ₄ H ₈ | -4,060 | 14,240 |
| <i>i</i> -C ₄ H ₁₀ | -32,200 | -4,720 |
| <i>i</i> -C ₈ H ₁₆ | -26,040 | 23,150 |
| <i>i</i> -C ₈ H ₁₈ | -54,610 | 2,820 |

Problem 24. Extrapolation of Heat-capacity Data to Low Temperatures. Using the following values for the molar-heat capacity of SnO₂, derive an equation for the heat capacity in terms of one Debye function and two Einstein functions:

| | | | | |
|------------------------|------|------|------|-------|
| Temperature, °K..... | 100 | 150 | 200 | 298.1 |
| C_p , cal./mole..... | 4.98 | 7.86 | 10.1 | 12.57 |

Compute the heat capacity of SnO₂ at 10, 25, and 50°K.

Problem 25. Heats of Sublimation from Vapor-pressure Data.—Using the following vapor pressures for $\text{PbS}_{(c)}$, compute the heat of sublimation of this compound at 900 and 1300°C.:

| | | | | | |
|-----------------------|-----|-----|-----|------|------|
| Temperature, °C..... | 850 | 910 | 940 | 980 | 995 |
| Pressure, mm. Hg..... | 2.0 | 4.1 | 6.0 | 12.0 | 17.0 |

The heat capacity of the solid is

$$C_p = 10.63 + 4.01 \cdot 10^{-3}T$$

and the fundamental vibration frequency of the gas equals 427 cm.^{-1} .

Problem 26. The ΔH and ΔF° of the Reaction, $\text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2$.—Derive equations for the ΔH and ΔF° of this reaction from the following data on heat capacities and observed SO_2 pressures:

| | |
|-------------------|--|
| SO_2 : | $C_p = 11.40 + 1.414 \cdot 10^{-3}T - 2.045 \cdot 10^{-5}T^{-2}$. |
| CaO : | $C_p = 10.00 + 4.84 \cdot 10^{-3}T - 1.080 \cdot 10^{-5}T^{-2}$. |
| CaSO_4 : | $C_p = 18.52 + 21.97 \cdot 10^{-3}T - 1.568 \cdot 10^{-5}T^{-2}$. |
| CaS : | $C_p = 10.00 + 4.84 \cdot 10^{-3}T - 1.08 \cdot 10^{-5}T^{-2}$. |

| | |
|------------------|--------------------------|
| Temperature, °K. | P_{SO_2} , atm. |
| 1173 | $5.26 \cdot 10^{-3}$ |
| 1233 | $2.50 \cdot 10^{-2}$ |
| 1273 | $5.40 \cdot 10^{-2}$ |
| 1313 | $1.09 \cdot 10^{-1}$ |
| 1353 | $2.03 \cdot 10^{-1}$ |
| 1393 | $3.13 \cdot 10^{-1}$ |

Compute ΔH and ΔF° at 298.1°K. for this reaction.

Problem 27. Derivation of Equation for C_p of Al_2O_3 .—Using 17.52 cal./deg. for the molar-heat capacity of Al_2O_3 at 0°C. and the following enthalpy data, compute the constants a , b , and c in the equation

$$C_p = a + bT - cT^{-2}:$$

| | |
|------------------|----------|
| Temperature, °K. | Enthalpy |
| 273.1 | 0 |
| 373.1 | 1,990 |
| 573.1 | 6,760 |
| 973.1 | 17,990 |
| 1173.1 | 24,220 |

Problem 28. Dissociation Constants of Weak Acids from Thermal Data. Calculate the three dissociation constants of H_3PO_4 from entropy data given in Appendix 5 and heats of formation given in Bichowski and Rossini. The entropy of $\text{H}_3\text{PO}_{4(aq)}$ equals 44 units.

Problem 29. Heat Content of Gaseous Ammonia at 25°C.—Calculate the heat content in excess of the zero-point energy of 1 mole of gaseous ammonia at 298.1°K. from the following data:

| Vibration Frequency, cm^{-1} | Degeneracy |
|---------------------------------------|------------|
| 964 | 1 |
| 1,630 | 2 |
| 3,336 | 1 |
| 3,300 | 2 |

Principal moments of inertia:

$$I_1 = 4.4 \cdot 10^{-40} \text{ g. cm.}^2$$

$$I_2 = I_3 = 2.79 \cdot 10^{-40} \text{ g. cm.}^2$$

Problem 30. The Free-energy Function for Gaseous Ammonia from Structural Data.—Compute the function $\frac{F^\circ - E_0^\circ}{T}$ for gaseous ammonia at 300, 600, and 1000°K. from the data given in Problem 29.

Problem 31. HCN from CO and Ammonia.—Discuss the feasibility of obtaining HCN via the following sequence of reactions:



Calculate a range of temperatures and pressures favorable to the formation of formamide in accordance with Eq. (1) and a range of temperatures and pressures favorable to the formation of HCN from reaction (2). Discuss possible complicating side reactions.

NOTE: The entropy of gaseous HCONH_2 may be estimated from procedures discussed in Chap. VIII.

Problem 32. The Temperature Coefficient of the Heat of Fusion of Ice.—The specific heat of ice is given by the equation

$$c_p = 2.1153 + 0.00779t \text{ international joules/g.}^\circ\text{C.}$$

The specific heat of liquid water equals 4.2177 absolute joules/g.°C. at 0°C., and the heat of fusion of ice equals 333.5 international joules/g. at 0°C.

Compute the temperature coefficient of the molar heat of fusion of ice at 0°C. using Eq. (2.33), and compare with the value obtained from the approximate Eq. (2.25). What is the entropy of fusion of ice?

Problem 33. The Free Energy of Gaseous Formaldehyde.—Calculate the ΔF° of formation of $\text{HCHO}_{(g)}$ from the following data:

$$\text{Heat of combustion} = 134,100 \text{ cal./mole.}$$

$$\text{Fundamental vibration frequencies} = 1,165, 1,278, 1,503, 1,750, 2,780, 2,875 \text{ cm.}^{-1}$$

$$\text{Interatomic distances: C} = \text{O distance} = 1.21 \text{ \AA.}$$

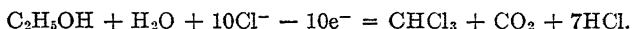
$$\text{C} - \text{H distance} = 1.09 \text{ \AA.}$$

$$\text{H} - \text{C} - \text{H} \angle = 120^\circ.$$

Problem 34. Electrolytic Reduction of Nitrobenzene to Aniline.—Estimate the kilowatt-hours required to produce 1 ton of aniline by cathodic reduction of nitrobenzene dissolved in strong acid. Assume a current

efficiency of 80 per cent and make reasonable assumptions as to overvoltages and cell resistance.

Problem 35. Electrolytic Production of Chloroform.—Estimate the kilowatt-hours required to produce 1 ton of chloroform by the anodic process in alkaline solution



The literature should be consulted in attempting to estimate overvoltages.

Problem 36. The Compressibility of a Mixture of Propane and *n*-Pentane. Using Kay's rule and Fig. 4, Chap. V, calculate the compressibility of a mixture of propane and *n*-pentane containing a mole fraction of pentane equal to 0.1468 at 121°C. and 27.2 atm. Calculate the volume occupied by 1 lb. of the mixture under these conditions. The following critical data are required:

| | T_c , °K. | P_c , atm. |
|---------------------------|-------------|--------------|
| C_3H_8 | 370 | 42.01 |
| C_5H_{12} | 470.3 | 33.04 |

NOTE: The measured compressibility factor for this mixture is 0.733.

Problem 37. The Heat of Hydrogenation of Ethylene.—An equimolar mixture of ethylene and hydrogen at 1 atm. is passed at a sufficiently slow rate over a hydrogenation catalyst so that the gas leaving the catalyst chamber may be assumed to be the equilibrium mixture corresponding to the catalyst temperature. Samples of this gas are withdrawn, cooled, and 100-cc. amounts introduced into an Orsat apparatus where the unsaturates are determined by absorption in fuming sulphuric acid. The following contractions in volumes were observed at the indicated hydrogenation temperatures:

| Temperature, °K. | $-\Delta V$, cc. |
|------------------|-------------------|
| 700 | 0.30 |
| 800 | 1.48 |
| 900 | 4.31 |

Compute the heat of hydrogenation of ethylene.

Problem 38. Single Electrode Potentials from Solubility Data.—The solubility of Ag_2SO_4 in water at 25°C. equals 0.0268 mole/liter, and the standard potential of the Ag ; Ag^+ electrode equals -0.80 volt. Calculate the standard potential of the Ag ; $\text{Ag}_2\text{SO}_4(c)$, SO_4^{--} electrode from these data. The Debye equation (Chap. V) may be employed for estimating the activity coefficient of the silver sulphate at these concentrations.

Problem 39. The Heat of Fusion of Silver from Freezing-point Data.—The solid phase in equilibrium with silver rich solutions of Ag-Zn is known to be a solid solution of these two components. Using the following data on temperatures at which crystallization in the melt is first observed and temperatures at which solidification is complete, derive a value for the atomic heat of fusion of silver:

| Mole fraction Ag, initial solution | Temperature of first crystal. °K. | Temperature of complete solid. °K. |
|--|--------------------------------------|--|
| 1.0000 | 1235 | 1235 |
| 0.8451 | 1145 | 1073 |
| 0.7744 | 1105 | 1015 |
| 0.7080 | 1039 | 993 |
| 0.6862 | 1023 | 983 |

Problem 40. The Fugacity of a van der Waals Gas.—The van der Waals constants for methane are

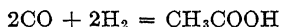
$$a = 2.504 \cdot 10^6 \text{ atm. cc.}^2 \quad b = 56.1 \text{ cc.}$$

Calculate the activity coefficient of methane at 200 atm. and 200°C. from these data and compare with the value obtained from Fig. 3, Chap. V. The critical temperature and pressure of methane are 190.7°K. and 45.8 atm., respectively.

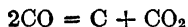
Problem 41. Graphical Calculation of Fugacity from *PVT* Data.—The most accurate procedure for evaluating fugacities depends on the use of measured *PVT* data in the required range of conditions. Using the following data on the specific volumes of gaseous ammonia, compute the fugacity of ammonia at 150°C. and 22 atm.:

| | | | | | | | | |
|----------------|-------|-------|-------|-------|--------|--------|-------|--|
| Pressure, p | | | | | | | | |
| atm. | 1.561 | 4.030 | 6.664 | 9.902 | 13.075 | 16.858 | 22.29 | |
| cc. per g. ... | 1,300 | 500 | 300 | 200 | 150 | 115 | 85.5 | |

Problem 42. Synthesis of Acetic Acid.—Discuss the possibility of producing acetic acid in accordance with the reaction

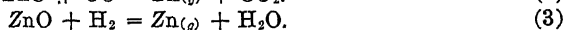
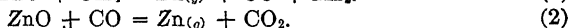
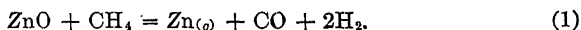


by computing the equilibrium conversions at 400, 700, and 900°K. at 100 and 300 atm. pressure for an equimolar mixture of CO and hydrogen. Possible side reactions resulting in the formation of methanol, methyl formate, methane, and formaldehyde should also be considered and the occurrence of the reaction



cannot be overlooked.

Problem 43. Reduction of Zinc Oxide with Methane.—Roasted zinc ores are usually reduced to metallic zinc by treatment with carbon. Investigate the possibility of using methane for this purpose by considering the following set of possible reactions:



Calculate the partial pressures of $\text{Zn}_{(g)}$, CH_4 , CO , CO_2 , H_2 , and H_2O in the equilibrium system when 1 mole of methane is contacted with 1 mole of ZnO at 1100 and 1200°K. at a total pressure of 1 atm. Assume that the system reaches equilibrium before an appreciable fraction of the methane is cracked into carbon and hydrogen.

NOTE: For the process to be operable it is necessary that the concentration of oxidizing agents (CO_2 , H_2O), that effect formation of "blue powder" (ZnO) on cooling, be very low.

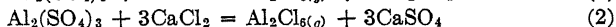
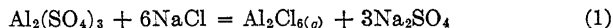
Problem 44. Heat Required for the Reduction of Zinc Oxide with Methane.—Estimate the gross heat required for the production of 1 ton of zinc by the process discussed in the preceding problem. Making reasonable assumptions regarding temperature gradients, estimate the quantity of heat conveniently recoverable by interchange; hence estimate the net heat required per ton of zinc. Assume the efficiency of CH_4 utilization equal 50 per cent.

Problem 45. Heat Required for Experimental Oil Cracker.—It is required to design a small, electrically heated laboratory unit for studying the thermal decomposition of hydrocarbons. If the oil stock to be used is essentially paraffinic and has a molecular weight of about 226 corresponding to hexadecane, estimate the kilowatt-hours required per pound of stock entering the unit at 25°C. As a first estimate assume that the maximum temperature for decomposition will be 900°C. and that the oil will decompose in about the following proportions:

| Weight Per Cent Stock Decomposed to | |
|---|---------|
| H_2 | 0.2 |
| CH_4 | 4.0 |
| $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ | 20.0 |
| $\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$ | 14.0 |
| $\text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10}$ | 8.0 |
| $\text{C}_8\text{H}_{16} + \text{C}_8\text{H}_{18}$ | Balance |

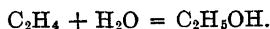
The ΔH of formation of liquid *n*-hexadecane equals $-109,780$ cal./g. mole.

Problem 46. Aluminum Chloride from Aluminum Sulphate.—Investigate the possibility of converting aluminum sulphate to aluminum chloride in accordance with the equations



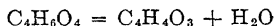
by calculating the equilibrium partial pressures of Al_2Cl_6 for both these systems at 400, 600, and 800°K. The ΔH and ΔF° of $\text{Al}_2(\text{SO}_4)_3$ at 25°C. are $-700,000$ and $-653,500$ cal., respectively. The entropy of CaCl_2 and Al_2Cl_6 may be estimated from the charts given in Chap. VIII.

Problem 47. Ethanol by Direct Hydration of Ethylene.—Deduce conditions of temperature and pressure likely to be favorable to the formation of ethanol from ethylene and water in accordance with the reaction



Both the gas-phase and liquid-phase hydration process should be considered and the effects of possible side reactions on the yields of alcohol considered. Discuss the merits of this process as compared to the indirect hydration process involving the absorption of C_2H_4 in concentrated H_2SO_4 followed by the hydrolysis of the ethyl sulphuric acid so formed.

Problem 48. Dehydration of Dibasic Acids.—The heats of combustion ($-\Delta H$) of crystalline succinic acid and succinic anhydride are 356,240 and 369,400 cal./mole, respectively, and the entropy of the acid equals 42.0 units at 25°C. Calculate the partial pressure of H_2O in the equilibrium system



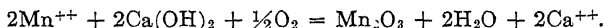
at 500, 600, and 700°K. On the basis of these calculations, does the straight thermal dehydration of the acid to the anhydride appear to be commercially feasible or would it be necessary to use powerful desiccating agents?

NOTE: See Sec. 3, Chap. VIII, for a discussion of a possible method for estimating the entropy of the anhydride.

Problem 49. Leaching Manganese Ores with Calcium Chloride Solutions.—In connection with the recovery of manganese from Chamberlain ores discussed in illustration 2, Chap. XV, consider the following possible process: (1) The ore is treated with a 40 weight per cent solution of $CaCl_2$ in order to dissolve the manganese. (2) The clear solution from (1) is treated with slaked lime and air in order to precipitate the manganese and regenerate the calcium chloride solution. (3) The mixture obtained in (2) is filtered in order to separate the hydrated, precipitated oxides from the regenerated leaching agent.

Calculate

- The gram moles of $CaCl_2$ plus kilograms of H_2O required to dissolve the $MnCO_3$ contained in 1 kg. of ore.
- The moles of $FeCO_3$ and $MgCO_3$ dissolved along with the manganese.
- The extent of completion of the regeneration reaction



NOTE: The entropy of unhydrated Mn_2O_3 may be estimated in accordance with the methods discussed in Chap. VIII.

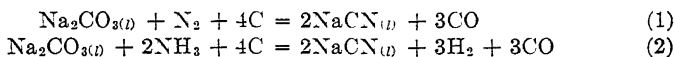
Problem 50. Design of Tower for Absorbing Ammonia under Isothermal or Adiabatic Conditions.—A mixture of air and ammonia, containing 7 per cent NH_3 (vol.) and about 2 per cent H_2O , is to be scrubbed countercurrently with water in a tower packed with $\frac{3}{4}$ -in. crushed stone, in order to recover the ammonia at 1 atm. pressure. The gas flow equals 650 lb./hr. (sq. ft. ground area) and the water flow equals 140 gal./hr. (sq. ft. ground area). If the water and air enter the tower at 20°C., calculate the height of the tower required in order to absorb 95 per cent of the ammonia, assuming isothermal operation. Calculate the height of the tower required to perform the same absorption under adiabatic conditions.

The absorption of ammonia in water at these concentrations liberates about 8,350 C.h.u./pound mole of NH_3 absorbed. Assume $K_p a$ for NH_3 equals 13 lb. moles/(hr.) (cu. ft.) (atm.) at these temperatures with absorp-

tion drives expressed as partial pressures of NH_3 in atmospheres. The over-all coefficient of heat transfer from the liquid to the gas phase may be taken equal to 100 C.h.u./(hr.) (cu. ft.) (deg. C.), and the transfer of water vapor may be neglected.

Problem 51. Design of Converter for Oxidizing Nitrosyl Chloride with Enriched Air.—Estimate the size of converter required to oxidize NOCl to within 80 per cent of the equilibrium value with a gas containing 40 per cent O_2 , plus 60 per cent N_2 , at 300°C . and 5 atm. pressure. The nitrosyl chloride is to be fed to the converter at the rate of 1 pound mole/(hr.) (sq. ft.) of converter cross section. Compare this result with the result obtained in illustration 1, Chap. XII.

Problem 52. The Formation of Sodium Cyanide from Soda Ash—I.—The two reactions



have been investigated as possible methods for the production of cyanides. Assuming that ΔC_p for reaction (1) is given by the approximate relation

$$\Delta C_{p(1)} = C_p(3\text{CO}) - C_p(\text{N}_2) - C_p(4\text{C}),$$

and that ΔC_p for reaction (2) is given by the equation

$$\Delta C_{p(2)} = C_p(3\text{H}_2) + C_p(3\text{CO}) - C_p(2\text{NH}_3) - C_p(4\text{C}),$$

derive equations for the ΔH 's of these two reactions as functions of temperature.

Estimating the entropy of $\text{NaCN}_{(c)}$ as 18 ± 3 units at 25°C ., derive equations for the standard free-energy changes of these two reactions as functions of temperature. Note the chosen standard states.

Problem 53. The Formation of Sodium Cyanide from Soda Ash—II.—Using the free-energy data derived in Problem 52, calculate the equilibrium constants for reactions (1) and (2) at 1100, 1200, and 1300°K .

Assuming that the reactants are contacted in stoichiometric proportions in static systems at a constant pressure of 1 atm., calculate the mole per cent soda ash converted to cyanide at equilibrium for both reactions at these three temperatures.

Assuming that the reactants could be contacted in stoichiometric proportions in countercurrent flow systems under 1 atm. pressure, what mole per cent conversions of the soda ash would be obtained at these temperatures? What would be the effect of using excess N_2 or NH_3 on the maximum yields obtainable in the flow system? What possible side reactions may occur in both cases?

Problem 54. The Formation of Sodium Cyanide from Soda Ash—III.—As a result of the calculations performed in Problems 52 and 53, estimate the optimum conditions under which to carry out reactions (1) and (2). Calculate the gross heat required to produce 1 ton of NaCN by both processes. Estimate the quantity of heat recoverable by interchange; hence

calculate the net heat required per ton of sodium cyanide. Which process do you favor? Why?

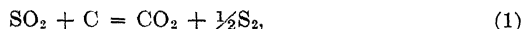
It should be noted that kinetic factors will be at least as important in this case as thermal and equilibrium considerations. Without actual rate data it is impossible to say whether reaction (1) or (2) will be the faster and which one will go at the lower temperature. Neither reaction will probably go rapidly or very far unless the reaction medium is a liquid in which the soda ash, carbon, and gas can be brought into intimate contact. This suggests that the lowest possible operating temperature will be the $\text{Na}_2\text{CO}_3 - \text{NaCN}$ eutectic temperature.

Problem 55. Flow of Dissociating Gases Accompanied by Large Temperature Drop.—Phosgene leaving a converter at 1.05 atm. pressure and 700°K ., enters a 20-ft. length of horizontal heat interchanger tubing where it is cooled to 450°K . If the internal diameter of the tubing equals 1.05 in., and the mass velocity equals 20,000 lb./(hr.)(sq. ft.), estimate the pressure drop in the tube.

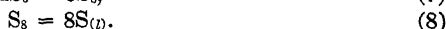
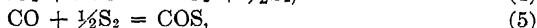
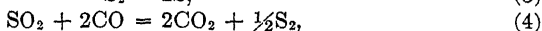
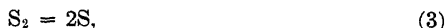
Owing to the fact that phosgene is appreciably dissociated at these temperatures into CO and Cl_2 , an added variable is introduced into the Bernoulli equation normally employed for solving such problems. The problem may, however, be handled by graphical integration when the degree of dissociation is known in the range of temperatures involved. Phosgene possesses the following fundamental vibration frequencies: 300, 302, 442, 573, 832, and $1,807\text{ cm.}^{-1}$

Problem 56. Heat Loss Accompanying Flow of Dissociating Gas.—Calculate the total heat that must be withdrawn per pound of phosgene under the conditions of temperatures, pressures, and flows specified in the previous problem. Calculate the total heat interchange per hour through the entire tube wall.

Problem 57. The Reduction of Sulphur Dioxide. I. Heats of Reaction.—The reduction of sulphur dioxide contained in smelter smoke by means of coke is an industrially important process. The main reactions involved are



and the secondary reactions are



Reaction (1) takes place rapidly at the surface of coke heated to 1400 to 1500°K ., and reaction (2) also takes place at these temperatures but at a slower rate. Reactions (3) and (4) also occur to a minor extent at these temperatures, although reaction (4) is used to "clean up" the unoxidized CO in the converter gases by passage over a catalyst (activated alumina)

at temperatures around 800°K. Reaction (5) occurs on cooling the gases from the hot zone to "clean-up" temperatures, and reactions (6) to (8) take place during the condensation of liquid sulphur from the converted gases.

Derive equations expressing the ΔH 's of reactions (1) to (7) as functions of temperature.

Problem 58. The Reduction of Sulphur Dioxide. II. Equilibrium Relations.—Derive equations for the standard free-energy changes of reactions (1) to (5) as functions of temperature and compute the equilibrium constants for these reactions at 800, 1100, and 1500°K.

Calculate the compositions of the gas mixtures obtained by passing gases of the following initial compositions through beds of coke at infinitely slow rates at these three temperatures and 1 atm. pressure:

| | Volume, per cent | | |
|-----------------|------------------|------|----|
| | | | |
| SO ₂ | 89 | 49.0 | 8 |
| O ₂ | 11 | 10.7 | 9 |
| N ₂ | .. | 40.3 | 83 |

Calculate the conversion of SO₂ [reaction (4)] at equilibrium when the three equilibrium mixtures corresponding to a reaction temperature of 1100°K. are permitted to reach equilibrium at 800°K. and 1 atm. pressure, after first adding unconverted gases to give a mole ratio of CO/SO₂ equal to 2.

Problem 59. The Reduction of Sulphur Dioxide. III. Thermal Requirements.—In order that reactions (1) and (2) of Problem 57 may be made to take place as rapidly as possible, it is necessary that the temperature of the reaction system reach 1400 to 1500°K. Assuming adiabatic operation and that the coke enters at 298°K., calculate the temperatures to which the three gas mixtures given in Problem 58 should be preheated in order to reach 1500°K. Coke may be assumed to contain 85 per cent carbon, plus 15 per cent ash, by weight.

On the basis of the following conditions and assumptions, estimate the tons of coke required per ton of sulphur produced by the reduction of each of the three gas mixtures given above:

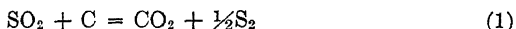
1. Continuous, countercurrent contacting of coke with gas.
2. Coke enters converter at 298°K., and gas at temperatures 100° greater than preheat temperatures computed for adiabatic operation.
3. Assume gases leave converter at 1100°K. and the SO₂ conversion corresponds to 95 per cent of the equilibrium value for this temperature.
4. Assume gases leaving the catalytic "clean-up" step [reaction (4)] are converted to 95 per cent of the equilibrium value for 800°K.
5. Assume heat leakage through walls of converter and unburned carbon in coke ash represents 10 per cent of the total enthalpy change of the system referred to 25°C.

6. Assume that the enthalpy of the gases leaving converter at 1100°K. is recoverable by heat interchange down to 450°K. The vapor pressure of sulphur at 450° equals 10^{-3} atm.

Calculate the additional heat per ton of sulphur that must be removed in order to condense completely the sulphur from the converted gases.

Problem 60. The Reduction of Sulphur Dioxide. IV. Converter Design. In order to obtain a preliminary picture of the gas flows, temperature gradients, and concentration gradients existing in the reduction converter, as well as the size of converter required for a given rate of sulphur production, it will be informative to set up differential equations expressing the partial pressures of SO_2 and CO_2 and the temperatures of the gas and coke as functions of the converter height (distance in coke bed above grate) when steady-state conditions prevail.

It will be necessary to assume that coke of a definite mesh size is being fed into the top of the converter at a definite rate, say 40 to 50 lb./ (sq. ft. of grate area)(hr.), and that a definite number of pounds of sulphur dioxide bearing gas enter the base of the converter per square foot of grate area per hour. In conformity with the known characteristics of the reaction of oxygen with coke it may be assumed that all of the O_2 is consumed within the first 4 in. of coke bed with the production of CO_2 and the evolution of a large amount of heat. From this point on, it will be necessary to assume that the primary reactions



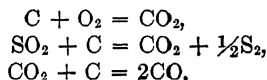
are the only reactions occurring in the system. Furthermore, it may be assumed that the rate of disappearance of SO_2 is equal to $k_1 P_{\text{SO}_2}$, whereas the net rate of CO_2 production equals $k_1 P_{\text{SO}_2} - k_2 P_{\text{CO}_2}$. The temperature dependence of k_1 and k_2 may be expressed in the usual manner by the equations

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \quad \text{and} \quad \frac{d \ln k_2}{dT} = \frac{E_2}{RT^2},$$

where the E 's represent energies of activation.

On the basis of the above assumptions, set up two differential equations for computing the coefficients dx/dh and dy/dh , where x represents the fraction of the inlet moles of SO_2 reduced, y represents the fraction of the inlet moles of oxygen (free plus combined) converted to CO_2 , and h is the distance above the grate in the converter.

In order to derive equations for calculating the gas and coke temperatures at any height h in the converter, it is necessary to set up an enthalpy balance that expresses the fact that the increase in sensible heat of the reactants over their inlet values, plus thermal leakage, must be equal to the net enthalpy increment produced by the chemical changes



Furthermore, the rate of heat transfer between the coke granules and the gas may be expressed in terms of the difference between the surface temperature of the coke and the temperature of the gas at the height h (assuming only vertical temperature gradients in the coke) and the over-all coefficient of heat transfer. The over-all solid-gas coefficient is compounded of a convection coefficient (h_c) and a radiation coefficient (h_r). Derive equations for computing the coefficients dt_g/dh and dt_c/dh , where t_g and t_c represent the temperatures of the gas and coke, respectively, at the height h . It will be noticed that stepwise, numerical integration of this set of four differential equations, based on the chosen rates of feed and preheat temperatures, permits the evaluation of all the necessary data on the performance of the converter within the accuracy of the stated assumptions.

In the event that you are unable to obtain approximate values for the various rate and heat-transfer coefficients required to solve these equations from the literature, devise small-scale laboratory experiments by means of which such values could be obtained, in order that a preliminary analysis of the performance of a reduction converter could be derived.

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